

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	1996	Conference Proceedings	
4. TITLE AND SUBTITLE Sixth International Conference on Composite Interfaces			5. FUNDING NUMBERS F6170896W0026
6. AUTHOR(S) Conference Committee			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Hebrew University of Jerusalem Jerusalem 91 904 Israel			8. PERFORMING ORGANIZATION REPORT NUMBER N/A
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) BOARD PSC 802 BOX 14 FPO 09499-0200			10. SPONSORING/MONITORING AGENCY REPORT NUMBER CSP 96-1001
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 words) The Final Proceedings for Sixth International Conference on Composite Interfaces, 5 May 1996 - 8 May 1996 Molecular interactions at interfaces, Structural Characterization, Theoretical aspects of the interfaces/interphases, interfacial adhesion: theory and applications, surface characterization techniques, surface treatments.			
14. SUBJECT TERMS BOARD			15. NUMBER OF PAGES
			16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102



International Conference on Composite Interfaces

MICROPHENOMENA IN ADVANCED INTERFACES

ICCI - VI

MORIAH GARDENS (GANEY CARMEL) HOTEL
ZICHRON YAACOV, ISRAEL

MAY 5-8, 1996

19990115 044

AQF99-04-0644

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SCIENTIFIC PROGRAM

SUNDAY May 5, 1996

20:00 - 21:00 Get-Together Reception at the Moriah Gardens (Ganey Carmel) Hotel.

MONDAY May 6, 1996

OPENING SESSION

9:00 - 9:15 Opening Comments by the co-Chairmen

Session Leader – M. Narkis

9:15 - 10:00 "Were McGarry or Shiriajeva right to measure glass fiber adhesion?" (Opening lecture)
J.-P. Favre (France)

10:00 - 10:30 "Probabilistic Analysis of the Single Fiber Fragmentation Test – Experiments and Simulations" (Invited lecture)
A. T. DiBenedetto (USA)

10:30 - 11:00 **Coffee**

11:00 - 11:30 "Fiber/matrix interface properties and the design of fiber coatings for ceramic composites" (Invited lecture)
R. Kerans (USA)

11:30 - 12:00 "Interfaces in metal matrix composites" (Invited lecture)
K. K. Chawla (USA)

12:00 - 12:30 "Surfaces, interfaces, interphases and "adhesion"" (Invited lecture)
L. Sharpe (USA)

12:30 - 14:00 **Lunch**

PARALLEL SESSION 1A: Polymer-polymer interfacial interactions

Session Leader – H. Schreiber

14:00 - 14:30 "Reactive blending for improving interfacial behavior" (Invited lecture)
L. Nicolais, E. Amendola, G. Giannotta, E. Occhiello, F. Garbassi (Italy)

14:30 - 14:50 "Mechanism of interface formation in organic composites based on polymer fibers"
V. I. Irzhak, L. I. Kuzub (Russia)

14:50 - 15:10 "Interface and polymer miscibility"
C. Thaumaturgo (Brazil)

15:10 - 15:30 "A physical method for enhancement of interfacial adhesion in polymer based composites: surface swelling and formation of an entangled brush layer"
Y. Cohen, D. M. Rein, L. E. Vaykhansky (Israel)

15:30 - 15:50 "Chemical interactions on interfaces and in interphases of microfibrillar composites from blends of condensation polymers"
S. Fakirov (Bulgaria)

15:50 **Coffee and Poster Time (session 1)**

PARALLEL SESSION 1B: Interfaces in ceramic and metallic composites

Session Leader – K.K. Chawla

14:00 - 14:30 "Interfacial and processing issues in ceramic matrix composites" (Invited lecture)
M. J. Koczak (USA)

14:30 - 14:50 "Transverse characterization of interfaces in continuously reinforced SiC/Ti-6Al-4V composites"
D. B. Miracle, S. Warrier, D. B. Gundel, B. Majumdar (USA)

14:50 - 15:10 "Stability of copper segregations on copper-carbon metal matrix composite interfaces under alloying"
S. Dorfman, D. Fuks (Israel)

15:10 - 15:30 "Interface degradation of an Al/C composite material under thermal cycling"
I. Ghorbel (France)

15:30 **Coffee and Poster Time (session 1)**

POSTERS: SESSION 1

1. "Interfacial phase separation in glass-fibre-reinforced composites based on blends of epoxy resin and commodity thermoplastics"
A. Saalbrink, T. Peijs, P.J. Lemstra (The Netherlands)
2. "Mechanical identification of interface conditions in composite materials"
P. Meurs, P. Schreurs, T. Peijs, H. Meijer (The Netherlands)
3. "The effect of adsorbed microspheres on the mechanical properties of model polymer matrix composites"
S. Ma, K.C. Opella, W.M. Cross, J.J. Kellar, R.M. Winter (USA)
4. "A simple fracture mechanics method for measuring the interfacial toughness with microbond tests"
J.A. Nairn (USA)
5. "Fibre fragmentation test with polyethylene composites"
F. von Lacroix, H. Wittich, K. Schulte (Germany)

6. "Morphological control in barium sulphate filled polypropylene/poly(styrene-co-acrylonitrile) blends"
C.O. Hammer, F.H.J. Maurer (Sweden)
7. "The influence of the curing process on the crazing level of filament wound laminates"
H. Dayan, A. S. Cherevatsky (Israel)
8. "The complex approach to the interphase phenomena in polymers: The new dimensionless adhesion-sensitive parameter of the respective monomers"
L.M. Pritykin (Ukraine)
9. "The effect of adhesion promotor layer thickness on the adhesion strength between silicone rubber and aluminum"
C. Ducso, T. Lohner, G. Banhegyi (Hungary)
10. "Low frequency acoustic scan analysis of morphology modifications of vinylester resins near a surface"
M. Nardin, X. Dirand, B. Hilaire, J.J. Hunsiger, B. Cros (France)
11. "Interfacial study in pitch-based carbon fibre/polycarbonate model composites"
M. Nardin, M.C. Paiva, C.A. Bernardo, J. Schultz (France/Portugal)
12. "Estimation of microcracking at the interfaces by X-ray determination of the strains in composites"
R. Khodakovskaya, E. Levi (Israel)
13. "High-strength and durable glass fibre reinforced cement"
N. Piven, N. Zaslavsky, M. Khodakovsky, A. Lifshits (Israel)
14. "Effect of the chain length of coupling agents on the silica-polyethylene adhesion"
J. Duchet, J.P. Chapel, B. Chabert, J.F. Gerard (France)
15. "Sawdust surface modification"
N. Marcovich, M.M. Reboredo, M.I. Aranguren (Argentina)
16. " Al_2O_3 - ZrO_2 composite coatings for thermal barrier applications"
P. Ramaswamy, S. Seetharamu, P.R. Krishnamoorthy, K.B.R. Varma, K.J. Rao (India)
17. "An electrochemical study on the behaviour of the metal-metalloid glass $(\text{Fe},\text{Cr})_{80}(\text{P},\text{C},\text{Si})_{20}$ in aqueous solutions containing chloride ions"
R. Kastner, K. Forkel, S. Rolle, M. Burghoff, F.G. Wihsmann (Germany)
18. "Metaillizing non-conductive surface by RF plasma technology"
T. Monetta, L. Nicodemo, F. Fracassi, R. d'Agostino, F. Bellucci (Italy)
19. "Fine scale processes on the interface of plastic fibre and polymer matrix"
R.A. Turusov, V. Arbouzov, D.I. Rublenko, V.I. Irzhack (Russia)
20. "The effect of loading in liquids on the adhesive strength of fibre-polymer systems"
V.G. Ivanova-Mumjieva, Yu.A. Gorbatkina, L.V. Puchkov, Z.P. Sulyaeva, G.S. Shul (Russia)
21. "Morphology of polyurethane grafts and blends"
M. Rutkowska, A. Eisenberg, H. Janik (Poland/Canada)
22. "A Mongrel finite element approach for interlaminar stress determination in multilayers composite laminates"
V. Michel, G. De Saxce (Belgium)

23. "Development of a surface topography on the metal-metalloid glass $(\text{Fe,Cr})_{80}(\text{P,C,Si})_{20}$, by an oxidative treatment and formation of a cement-reactive surface layer investigated by REM/EDXA"
K. Forkel, S. Rolle, F.G. Wihsmann, P.J.M. Bartos (Germany/UK)

24. "Discrete models of failure for particulate rubber composite"
V.V. Moshev, S.E. Evlampieva (Russia)

25. "On estimation of adhesive bond strength"
R.A. Turusov, Yu.A. Gorbatkina (Russia)

26. "Effect of interlayer between amorphous and crystalline phases on the mechanical and thermoelastic behaviour of poly(aryl ether ketones)"
A. Tregub (USA)

27. "Effects of silane coupling agents on interphase and performance in glass-fiber reinforced composites"
H.F. Wu, N.T. Huff, D.W. Dwight, K.D. Baumgard, A.P. Diwanji (USA)

28. "Self-rearrangement of the transition composition zone of polymer-metal joints in water"
V.V. Arslanov, I.V. Kalashnikova, V.V. Matveev, I.A. Gagina (Russia)

29. "Surface reconstruction of photooxidized EPDM rubber: Kinetics and mechanism"
V.M. Rudoy, V.A. Ogarev (Russia)

30. "The role of interfacial debonding in fatigue of polymer composites"
K. Gamstedt, L.A. Berglund (Sweden)

31. "Identification of the Young's modulus of the interphase in glass/epoxy composites"
G. Wacker, A. Chate, A.K. Bledzki (Germany)

32. "Short aramid-fiber reinforced ultra-high molecular weight polyethylene"
J.M. Hofste, A.J. Pennings (The Netherlands)

33. "Model polycondensates for the matrix-glassfiber interphase I) humid ageing of systems containing amine, epoxide or alkyl groups"
L. Salmon, F. Thominette, J. Verdu, M.F. Pays, D. Paris (France)

34. "Influence of graft lengths on adherence and moisture aging in cellulosic fibre/polypropylene microcomposite"
C. Joly, M. Escoubes, R. Gauthier, B. Chabert (France)

35. "Characterization of the fibre-matrix interface with the indentation technique"
G. Kalinka, A. Leistner, A. Hampe (Germany)

36. "Effect of sizing agent on interfacial properties of aramid knitted structural composites"
K. Kitagawa, H. Hamada, N. Ikuta (Japan)

37. "Characterization of the Lewis acid base behaviour of modified polyolefine surfaces by means of flow sorption microcalorimetry and inverse gas chromatography"
S. Schneider, H.J. Jacobasch (Germany)

PARALLEL SESSION 2A: Adhesion at interphases

Session Leader – C. Galiotis

8:30 - 9:00 "The polymer interphase in composites: intrinsic limitations to adhesion"
(Invited lecture)
L. T. Drzal (USA)

9:00 - 9:20 "Specific coupling agents for promoting adhesion between conductive polypyrrole and glass fibers surface"
A.-J. Attias, F. Faverolle, O. Le Bars, B. Bloch (France)

9:20 - 9:40 "Plasma treatment and adhesion properties of impact-modified polypropylene"
A. Nihlstrand, T. Hjertberg, H. P. Schreiber, J. E. Klemberg-Sapieha (Sweden/Canada)

9:40 - 10:00 "A pseudo energy based method to predict fiber-matrix adhesion using a single filament composite"
D. Tripathi, F.R. Jones (UK)

10:00 - 10:20 "Observation of two glass transitions in filled polymers"
G. Tsagaropoulos, A. Eisenberg (Canada)

10:20 - 11:00 **Coffee**

PARALLEL SESSION 2B: Interfaces in ceramic and metallic composites

Session Leader – M.S. Koczak

8:40 - 9:05 "Study of microstructure and interfacial properties of composite materials prepared with alkali resistant silicate glass fibers and alinite cement and other hardened cementitious matrix materials"
F. G. Wihsmann, K. Forkel, R. Stodolski, S. Rolle (Germany)

9:05 - 9:30 "The role of the interface in brazed metal/ceramic laminate"
D. Sherman (Israel)

9:30 - 9:55 "Evaluation of the interfacial bonding properties in different gradation for C/C composites"
Y. D. Huang, W. X. Sun, Z. Q. Zhang, J. S. Wang, Y. Z. Wei (P. R. China)

9:55 - 10:20 "Ca segregation to basal α -alumina surfaces and its role at metal-ceramic interfaces"
W. D. Kaplan, H. Mullejans, M. Ruhle (Israel/Germany)

10:20 - 11:00 **Coffee**

PARALLEL SESSION 3A: Surface treatments

Session Leader – C. Schutte

11:00 - 11:30 "Silane coupling functions and fracture of composites" (Invited lecture)
N. Ikuta (Japan)

11:30 - 11:50 "Fiber surface modification in glass-epoxy pultrusion"
M. Ambrustolo, S.M. Moschiar, M.M. Reboreda, A. Vazquez (Argentina)

11:50 - 12:10 "Plasma polymerisation for molecular engineering of carbon fibre surfaces for optimised composites"
A.P. Kettle, A.J. Beck, F.R. Jones, R.D. Short, L. O'toole (UK)

12:10 - 12:30 "Surface treatment and modifications of natural fibres in polymer matrix for the development of wood substitute in building constructions"
A.C. Khazanchi (India)

12:30 - 12:50 "Surface modification of UHMWPE fibres and films through plasma etching or plasma polymerization"
M.S. Silverstein, D. Alon, J. Sadovsky (Israel)

13:00 - 14:30 **Lunch**

PARALLEL SESSION 3B: Interface characterization

Session Leader – T. Peijs

11:00 - 11:30 "Positron annihilation in polymers and composites" (Invited lecture)
F. Maurer (Sweden)

11:30 - 11:50 "In-situ near IR interphase cure monitoring of model polymer matrix composite materials"
S.L. Cossins, M.E. Connell, W.M. Cross, J.J. Kellar, R.M. Winter (USA)

11:50 - 12:10 "Characterization of the interphase in twaron aramid fiber applications"
J. Mahy (The Netherlands)

12:10 - 12:30 "Study of fiber surface treatments for control of interphase properties in composites"
E. Maeder (Germany)

12:30 - 12:50 "Fundamental studies of fiberglass in composites"
D.W. Dwight (USA)

13:00 - 14:30 **Lunch**

PARALLEL SESSION 4A: Stress transfer at interfaces

Session Leader – M. Nardin

14:30 - 15:00 "Stress analysis of the fragmentation test including the effect of an imperfect interface: application to interpretation of experimental results" (Invited lecture)
J.A. Nairn (USA)

15:00 - 15:20 "Shear stress distribution in the fiber-matrix interface during load transfer"
B. Fiedler, K. Schulte (Germany)

15:20 - 15:40 "The adhesive strength of fiber-matrix interface upon cyclic action of low temperatures: the effect of joint preparation conditions"
Yu. A. Gorbatkina, Z.P. Suliaeva, V.G. Ivanova-Mumjieva (Russia)

15:40 - 16:00 **Coffee**

16:00 - 16:20 "Effect of interface upon the tensile fracture of unidirectional composites"
C. Galiotis, V. Chohan, C. Marston (UK)

16:20 - 16:40 "The toughness of the fiber/matrix interface measured by the single fibre pull-out test"
A.H. Hampe, C. Marotzke (Germany)

16:40 - 17:00 "The effect of moisture on the relative durability of both glass fibers and fiber/matrix interfaces using the single fiber fragmentation test"
C. Schutte (USA)

17:00 **Coffee and Poster Time (session 2)**

PARALLEL SESSION 4B: Microstructure of interlayers

Session Leader – L.T. Drzal

14:30 - 14:50 "Fractal nature of interfaces in composites: observation, characterization, and mechanical implications"
Y.A. Dzenis (USA)

14:50 - 15:10 "Crystallization analysis at carbon fiber/PEKK interfaces in model composites"
M. Nardin, E.M. Asloun, J. Schultz (France/Morocco)

15:10 - 15:30 "Contribution of crystallinity on the interfacial strength in thermoplastic composites"
J. Denault, J. Guillemenet (Canada)

15:30 - 16:00 **Coffee**

16:00 - 16:20 "Tailoring the interphases in carbon or glass-poly(phenylene sulfide) systems by controlling the growth of transcrystalline layers or by using polymeric co-coupling agents"
L. Gonon, L. Caramaro, B. Chabert, J.F. Gerard (France)

16:20 - 16:40 "The effect of transcrystallinity upon interfacial micromechanics in polymer matrix composites"
M. Heppenstall-Butler, R.J. Young (UK)

16:40 - 17:00 "Functionally gradient type of polymer composites"
C.R. Choe, M. Park (Korea)

17:00 **Coffee and Poster Time (session 2)**

POSTERS: SESSION 2

38. "Study on wetting between glass fibres and polypropylene melts using the Wilhelmy technique"
K. Grundke, T. Gietzelt, B. Redlich, E. Maeder, H.J. Jacobasch (Germany)
39. "Embedded Single fibre dynamic load test as a method for interphase characterization"
E. Maeder, K. Mai (Germany)
40. "Polymers grafted cationically on silica surfaces"
F. Simon, H.J. Jacobasch, S. Spange, J.P.S. Badyal (Germany/UK)
41. "Dielectric investigations on HDPE/CaCO₃ compounds-structures of the interfaces"
J. Luhr, F. Janowski, H. Thiel (Germany)
42. "Reinforcement of elastic modulus in ultrafine particle filled polymers"
M. Kryszewski, G.W. Bak (Poland)
43. "A novel single polymer composite material consisting of ultra-high molecular weight polyethylene fibers and matrix"
Y. Cohen, D.M. Rein, L.E. Vaykhansky (Israel)
44. "Weight change analysis of the interphase in hydrothermal aged FRP: consideration of debonding"
T. Morii, N. Ikuta, K. Kiyosumi, H. Hamada (Japan)
45. "Effects of thermal treatments on the interfacial shear strength of nylon-6-glass and carbon fiber composites"
A. Pegoretti, L. Fambri, C. Migliaresi (Italy)
46. "Adhesion strength of fibrous composite: Analytical study and comparison with experiments"
L.I. Manevitch, A.V. Pavlenko (Russia)
47. "On the transition between microhomogeneous and craze-like mechanisms of debonding in particulate composites"
V.G. Oshmyan, D.K. Muravin (Russia)
48. "Deformation micromechanics in polyethylene/epoxy composites using Raman spectroscopy"
P.I. Gonzalez-Chi, R.J. Young (UK)
49. "Fractography of fracture aspects in CFRP"
Y. Nakanishi, K. Hana, H. Hamada (Japan)
50. "Delamination of glass woven fabric composites under Mode I loading"
M. Kotaki, H. Hamada (Japan)
51. "Evaluation of fiber/resin interface inside of fiber bundles"
H. Hamada, M. Kotaki, Y. Hirai, K. Hana (Japan)
52. "Diacetylene containing urethane copolymers for strain measurement applications in glass fibre composites"
C. Thongpin, R.J. Young, J.L. Stanford, P.A. Lovell (UK)
53. "On the thermodynamic definition of surface stress"
E.M. Gutman (Israel)

54. "Moisture absorption and ageing of interfaces in epoxy matrix composites"
D.J. Bannister, A.J. Cervenka, R.J. Young (UK)

55. "The effect of the surface morphology, network structure and chemical modification of vulcanized scrap rubber powder on the performance of the tire tread"
M. Tu, M. Zhu, X.-D. Wu (China)

56. "Influence of surface treatment on mechanical properties and crystallization of GF/PP film stacking composites"
H. Hamada, Y. Murano, M. Kotaki (Japan)

57. "Interactions between neighbouring fibers in multi-fibre composites: The presence of matrix cracks"
A.L. Buxton, C.A. Baillie (Australia)

58. "On the mechanism of thermoplastic matrix/single glass fibre microcomposite failure"
E.V. Pisanova, S.F. Zhandarov (Belarus)

59. "The local bond strength and its determination by the fragmentation and pull-out tests"
S.F. Zhandarov, E.V. Pisanova (Belarus)

60. "Assessment of influence of interfacial properties on stress transmissibility in composite by numerical approach"
K. Nishiyabu, A. Yokoyama, H. Hamada (Japan)

61. "Impact damage and resistance of quasi-isotropic wet and dry T300/914C laminates"
B. Qi, I. Herszberg, K.H. Leong, A.A. Baker, M. Bannister (Australia)

62. "Surface damage characterization of carbon-carbon composite materials in braking application"
Y. Remond, C. Wagner (France)

63. "Phenomenological analysis of microphase separation region in relation with SAXS investigations of polymer blend fibres"
A. Wlochowicz, J. Janicki, M. Linek, C. Slusarczyk (Poland)

64. "Characterization of interfaces in composite materials by optical fiber sensing"
A. Mittelman, I. Roman (Israel)

65. "Origin, morphology and crystallography of transcrystallinity in polyethelene-based single polymer composites"
T. Stern, G. Marom (Israel)

66. "Assessing the effects of fibre sizing, material processing and temperature upon the stress- transfer characteristics in model composites"
A. Paipetis, C. Galiotis (UK)

67. "The change of the morphology of the fibres on the basis of the poly(ethylene terephthalate) – fibre in mixtures in the strained process above the glass temperature of matrix polymer"
B. Geller (Belarus)

68. "Interfacial adhesion in the presence of water"
T. Weinberger, H.D. Wagner (Israel)

69. "Microphenomena in advanced composites: Review of energy-based interpretations of interfacial adhesion"
O. Lourie, X.-F. Zhou, H.D. Wagner (Israel)

70. "Transcrystalline interphases: New microindentation and AFM results"
E. Amitay-Sadovsky, H.D. Wagner (Israel)

71. "Study of the effect of transcrystallinity in Kevlar 149-poly(caprolactone) composites by means of the microbond test"
A. Gati, H.D. Wagner (Israel)

72. "Structural inhomogeneities of liquid epoxy resin"
M.R. Kiselev, I.I. Bardyshev (Russia)

73. "The role of interfacial tension in production of asphalt pavings and cement concrete"
K.G. Ohlson (Sweden)

74. "Slow positron spectroscopy: A non-destructive alternative to peeling tests for adhesion assessment"
R.I. Grynszpan, P.G. Coleman, T. Tatoulian, F. Arefi-Khonsan, J. Amouroux (France/UK)

75. "Effects of fiber coatings on static and impact mechanical properties of glass reinforced composites"
R. Podgaiz, R. Williams (Argentina)

76. "An analytical approach to optimum adhesion in fibre reinforced composites"
M.T. Connor, J.-E. Bidaux, J.-A.E. Manson (Spain/Switzerland)

77. "The role of the interface in the compressive behaviour of interply hybrid composites"
J.F. Harper, S.J. Michiels (UK)

78. "Prediction of interfacial strength distribution using a single-fibre composite test"
A.T. Dibenedetto, M.R. Gurvich (USA)

79. "Microwave properties in the x-band and some tensile properties of carbon fibre-polypropylene and carbon-black-polypropylene composites"
A. Kaynak, U. Yilmazer (Turkey)

80. "Effect of interface on degradation of glass fiber/vynilester composites"
A. Tregub, I. Tregub, V.M. Karbhari (USA)

SESSION 5 (evening): Fundamentals of interface adhesion

Session Leader – R.S. Young

19:30 - 20:00 "Adhesion measurement and interpretation" (Invited lecture)
K. Kendall (UK)

20:00 - 20:30 "Fundamental studies of interfacial shear between solid surfaces" (Invited lecture)
J. Klein (Israel)

8:15 - 9:00 **Plueddemann Award (Invited lecture)**

PARALLEL SESSION 6A: Effects of interfaces on composite properties (I)

Session Leader – H.F. Wu

9:00 - 9:20 "The effect of absorbed moisture on damage development in polymeric composites"
W.L. Bradley, C. Wood, C. Chatawanich (USA)

9:20 - 9:40 "Heterogeneous phase separation around fibers in epoxy/PEI blends and its effect on composite delamination resistance"
D.J.-P. Turmel, I.K. Partridge (UK)

9:40 - 10:00 "Upper-bound analysis of interfacial effects on transverse failure initiation in polymer composites"
L.E. Asp, L.A. Berglund (Sweden)

10:00 - 10:20 "Micromechanical aspects of crack bridging in aramid/epoxy composites"
J.A. Bennett, R.J. Young (UK)

10:20 - 11:00 **Coffee**

PARALLEL SESSION 6B: Interfacial micromechanics (I)(#)

Session Leader – L.A. Berglund

9:00 - 9:25 "Theoretical consideration of the single-fibre pull-out test"
W. Beckert, B. Lauke (Germany)

9:25 - 9:50 "Influence of the thermal history on the results of fragmentation test of high modulus carbon fiber-polycarbonate model composites"
M.C. Paiva, M. Nardin, C.A. Bernardo, J. Schultz, A. Ramos (Portugal/France)

9:50 - 10:25 "Interfacial crack propagation with friction arising in single fiber pull-out tests"
C.G. Marotzke, L. Qiao (Germany)

10:25 - 11:00 **Coffee**

PARALLEL SESSION 7A: Effects of interfaces on composite properties (II)

Session Leader – A. Weinberg

11:00 - 11:30 "Role of interfaces in mode II fatigue delamination growth of interlayer toughened graphite/epoxy laminates"
I. Kimpara, K. Kageyama, Z.-W. Li, I. Ohsawa, T. Suzuki (Japan)

11:30 - 12:00 "Micromechanical study of the influence of interfacial failure on the macroscopic behaviour of composites"
J. Fitoussi, G. Guo, D. Baptiste (France)

12:00 - 12:30 "Thermal residual stresses in single fiber polymer composites"
A. Pegoretti, M. Detassis, C. Migliaresi, H.D. Wagner (Italy/Israel)

12:30 - 13:00 "The effect of fiber surface treatment on its strength and adhesion to the matrix"
I.A. Rashkovan, Y.G. Korabelnikov (Russia)

13:00 - 14:30 **Lunch**

PARALLEL SESSION 7B: Interfacial micromechanics (II)(#)

Session Leader: S.L. Phoenix

11:00 - 11:25 "Determination of the interfacial fracture toughness of composites by the use of fragmentation test" (Invited lecture)
I. Verpoest, T.J. Copponex, M. Desaeger (Belgium)

11:25 - 11:50 "Tensile fracture of fibre-polymer interfaces"
M.R. Piggott (Canada)

11:50 - 12:15 "Interfacial micromechanics of graphite/epoxy composite compression stresses: A micro-Raman spectroscopic study"
M.S. Amer, M.J. Koczak, L.S. Schadler (USA)

12:15 - 12:40 "Time and temperature effects on interfacial shear stress using the microbond test"
A. Straub, P. Schwartz (USA)

12:40 - 13:00 "The role of the interface in the toughness of polypropylene-glass composites"
E.D. Williams, L.S. Schadler, A. Lustiger (USA)

13:00 - 14:30 **Lunch**

SESSION 8: Interfacial micromechanics (III)(#)

Session Leader – A.T. Dibenedetto

14:30 - 14:50 "An experimental and numerical investigation into the influence of fibre/matrix adhesion on stress enhancement in carbon/epoxy microcomposites"
P.W.J. van den Heuvel, T. Peijs (*The Netherlands/UK*)

14:50 - 15:10 "Interfacial measurements in carbon fibre epoxy composite tows using the technique of laser Raman spectroscopy"
C. Marston, B. Gabbitas, J. Adams, C. Galiotis (*UK*)

15:10 - 15:30 "Statistical fracture behavior of a fiber-reinforced composite containing Weibull fibers, yielding matrix, and debonding fiber-matrix interface"
I.J. Beyerlein, S.L. Phoenix (*USA*)

15:30 - 16:00 **Coffee**

16:00 - 16:20 "A new evaluation method of fiber/resin interface by using fiber strand"
K. Hana, M. Kotaki, H. Hamada (*Japan*)

16:20 - 16:40 "Simulation of crack propagation along interfaces in composite materials"
J.K. Burton Jr., S.L. Phoenix (*USA*)

16:40 : CLOSURE COMMENTS – I. Verpoest

(#) We wish to thank the United States Air Force European Office of Aerospace Research and Development for its contribution to the success of Sessions 6B, 7B, and 8 on Interfacial Micromechanics.

ABSTRACTS

Opening Session

WERE McGARRY OR SHIRIAJEVA RIGHT TO MEASURE GLASS FIBERS ADHESION ?

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According to the author's knowledge, fibre adhesion to organic matrices was first measured reproducibly in terms of bonding strength around 1960-1962...

Since then fibre/matrix interface and related microphenomena in all composite families have been thoroughly investigated. With ups and downs. Examples will be given of the success of concepts and methods for material characterization, providing useful guidelines for composite tailoring and design but also of the difficulties in the mechanical analysis and integration of relevant parameters into effective models of composite behaviour.

PROBABILISTIC ANALYSIS OF THE SINGLE FIBER FRAGMENTATION TEST - EXPERIMENTS AND SIMULATIONS

INVITED LECTURE at ICCI-VI , May 5-8 1996 , ZICHRON, ISRAEL

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The utility of micromechanical measurements depends in part on the ability of different laboratories to calculate comparable values of the interfacial shear strength and the debonding fracture energy. One of the most common tests utilized for this purpose has been the embedded single fiber fragmentation test. Both analytical and numerical solutions have been proposed to relate fiber fragment distributions to an average interfacial shear strength , τ , and to evaluate an interfacial debonding energy, G . All of these analyses are limited by the assumptions required for calculation of the properties. While significant advances in understanding have accrued over the years, a recent round robin experimental study of average interfacial shear strength using four different test techniques made it clear that the present test procedures do not provide a consistent method of evaluating microcomposite properties. The scatter of results using a particular test method within each laboratory were often acceptable, but the scatter between laboratories was unacceptably high. It is our premise that both τ and G are statistical properties of the fiber/matrix interface and that in the absence of a standardized probabilistic analysis of the problem, uniformity of results is unlikely. In a recent study, for example, we have shown that the statistical parameters chosen to characterize fiber strength have a large effect on calculated values of the average interfacial shear strength. We presume that other potential sources of material property variations, such as non-uniformity of the interface, the debonding and/or matrix cracking that accompanies each fiber fracture and variability of the fiber diameter, will create a similar uncertainty in calculated values of τ and G .

A probabilistic model and computational strategy for analysis of fiber fragmentation distributions in a single fiber composite* will be presented. The effect of interfacial debonding and the statistical parameters of a Weibull distribution of fiber strength on the average fragment length and its variability will be considered. In addition, a procedure for evaluation of Weibull parameters utilizing data on *in-situ* fiber strength will be suggested. Implementation of the probabilistic strategy will result in a calculation of statistical parameters for characterization of an average τ and its variability.

*** A.T. DiBenedetto, M.R. Gurvich, *Statistical Simulation of Fiber Fragmentation in a Single Fiber Composite*, submitted for publication in Composite Science and Technology, 1996.**

Abstract for invited lecture at the conference ICCI-VI, Zichron Yaacov, Israel, 5-8 May 1996.

FIBER/MATRIX INTERFACE PROPERTIES AND THE DESIGN OF FIBER COATINGS FOR CERAMIC COMPOSITES.

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While it has long been appreciated that fiber/matrix interfacial mechanical properties are a major determinant of the properties of ceramic composites, recent work has indicated that the possible range of those properties is much broader than previously believed. This has delineated inadequacies in our understanding of composite behavior and in our ability to measure interface properties. However, it has also expanded the range of possible approaches to interface control. This is a most welcome development because oxidation resistant interface control is the limiting technology in the application of ceramic composites. These issues will be surveyed and the implications regarding coating design will be discussed.

INTERFACES IN METAL MATRIX COMPOSITES

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ABSTRACT

Interface region in a given composite has a great deal of importance in determining the ultimate properties of the composite. An interface is, by definition, a bidimensional region through which there occurs a discontinuity in one or more material parameters. In practice, there is always some volume associated with the interface region over which a gradual transition in material parameter(s) occurs. The importance of the interface region in composites stems from two main reasons: (i) the interface occupies a very large area in composites, and (ii) in general, the reinforcement and the metal matrix will form a system that is not in thermodynamic equilibrium. I shall give examples of the interface microstructure in different metal matrix composite systems (particle and fiber reinforced as well as laminates) and discuss some of the important implications on various aspects of metal matrix composites, from the processing stage to ultimate performance of the composite.

SURFACES, INTERFACES, INTERPHASES AND "ADHESION"

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It is well known that materials in contact with each other influence, e.g., the structure and/or composition and/or properties of one or both materials in the near-interface region--most commonly called the interphase. The mechanisms that produce interphases are many and varied so it is probably true that interphases are almost always present where two materials join. Therefore, it is probably misleading to speak about the "interfacial shear strength" of a composite material or structure (such as an adhesive joint). This is not a trivial matter, as language influences perception. In this case, it leads to the perpetuation of the concept of true "interfacial failure"--a highly unusual occurrence--thus, also, to the concept of "interfacial strength", as if it were a parameter related to the surface energetics of a material combination, independent of the geometry and mechanical properties of the materials in the combination and of the interphase.

In this connection, It will be shown that the behavior of a rubber/metal joint system which, in its initial geometry, exhibits "weak" behavior (and "interfacial" failure) can be made to exhibit "strong" behavior (and "cohesive" failure) simply by introducing a certain kind of flaw into the joint. Such experimental evidence suggests that it is unwise to draw direct, simple, cause and effect relationships between interfacial interactions and macroscopic joint performance. An alternative explanation is given for the joint's behavior.

Two other topics which bear re-examination as to their usefulness will also be presented and discussed. The first is the concept of, and a model for, a roughness-created interphase, put forth by the author more than 20 years ago. To the author's knowledge, the concept has never been suitably explored. A second is the matter of conservation of material during joint failure. The results of experiments with a particular joint system will be presented. These clearly show that, for this system, material is ejected from the joint during failure. Such behavior, unless it is specifically ruled out, raises some doubts about the credibility of fractographic evidence and, thus, the conclusions drawn from it.

Session 1A

REACTIVE BLENDING FOR IMPROVING INTERFACIAL BEHAVIOR

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Multicomponent polymer blends, for improving both process and product related properties, often require the optimization of interfaces/interphases. This is particularly true in the case of blends based on recycled polymers.

Beside a review of existing approaches, two examples will be presented in more detail. The former will be related to the toughening of recycled PET (poly(ethylene terephthalate) by reactive ethylene-ethyl acrylate-glycidyl methacrylate elastomers. The effect of catalysts of the reaction between elastomer epoxide functions and PET carboxyl and hydroxyl end-groups and of impurities introduced during recycling has been assessed. Variations of rheological behaviour, morphology of chips and molded parts, mechanical properties have been characterized and related to interfacial chemistry. The formulation with glass fibers has also been experimented with and interesting informations on the compromise between resilience and rigidity have been acquired.

The second example is related to the so called "light fraction" of recycled polymers, including mainly polyethylene and polypropylene. Mixing has been performed in various relative amounts, as such and in the presence of initiators inducing both bulk and interfacial radical reactions. Effects on rheology, morphology and mechanical properties have again been assessed, observing that the initiation of reactions is an important tool for improving interfacial behaviour.

MECHANISM OF INTERFACE FORMATION IN ORGANIC COMPOSITES BASED ON POLYMER FIBERS

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The main mechanism of interface formation in organic composites based on polymer fibers is shown to be sorption interaction of the latter with binder components. This interaction takes place during the process of composite formation: wetting and impregnation of the fibers with the binder components followed by curing. As a result the expanded interface layer is formed. It consists generally of the fiber skin layer modified by sorption and possible curing of sorbed binder components. Its properties are depended on the concentration and conversion of the sorbed components. Therefore, just the sorption properties of the fiber skin layer determine the structure and properties of formed interface layer.

In the work there are data on sorption behavior of some polymer fibers: aramide (type of Kevlar) and polyethylene (type of Spectra).

The studies of sorption kinetics of low molecular sorbates with aramides fibers showed that the specific heat of sorption changed in the process: while passing the skin layer specific heat increased and then did not change practically. The diffusion coefficient decreases at time and its value for fiber skin was higher as compare with one for fiber core. Methods of isothermal calorimetry and inverse gas chromatography allowed to evaluate the thickness of skin layer: it was equal about 0.1 of fiber radius. So, it was reasonable to consider the thickness of the interface layer to be the same.

Sorption of low molecular substances led to alternation in some degree of the skin layer structure. This conclusion was obtained from analysis of data on the temperature dependence of mechanical losses been measured with braid pendulum. In the method the unconnected bunch of the fibers was used as the pendulum string. Therefore, the external friction of the fiber surfaces was the main source of the mechanical losses. At the same time temperature of the main relaxation transitions in surface layer were lower than ones of fibers in average. So, the skin layer was more disordered and less dense than core of polymer fibers. These results were supported by experimental data on thermomechanical analysis obtained on unconnected fiber bunch been deformed in transversal direction.

Investigation of the initial stage of rupture of the model composites based on monofilament allows us to assume that interface has more rigid structure than the fiber: just the interface is that place where crack initiation occurs generally. Probably, higher rigity is caused by the curing processes taken place in the interfaces.

INTERFACE AND POLYMER MISCELLITY

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ABSTRACT

The study of the interface in polymer blends gives useful information about the thermodynamical miscibility of the system. The surface tension of the pure EVA copolymers shown that the acetate content plays the main role. It is also reflected on the interfacial tension of the PVC blends. The results shown a direct relationship between the interface thickness and the vinyl acetate content in EVA copolymer. Interaction parameters values presented an inversely related correlation. Calculated values obtained from the adequate equations shown small discrepancies from experimental data. The Flory-Huggins parameters theoretically calculated using the recent theories which suppose that the vitreous transition is a true transition, are in good agreement with the values obtained from calorimetric measurements.

A PHYSICAL METHOD FOR ENHANCEMENT OF INTERFACIAL ADHESION IN POLYMER BASED COMPOSITES: SURFACE SWELLING AND FORMATION OF AN ENTANGLED BRUSH LAYER

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The material properties of ultra-high molecular weight polyethylene (UHMWPE) and of high-performance fibers fabricated from it are unique among polymeric materials which exhibit high modulus and strength. However, the joint utilization of these UHMWPE components in a composite material has not been successful as yet. A major deficiency is the chemical inertness of UHMWPE and hence the relatively poor adhesion between fiber surface and matrix.

We successfully investigated a physical method for improvement of the interfacial adhesion between UHMWPE fibers and the same polymer matrix, based on the following physical processes:

- a. Surface swelling of UHMWPE fiber under tension in a hot UHMWPE solution;
- b. Growth of brush layers from dissolved UHMWPE molecules entangled with the swelled UHMWPE fiber surface;
- c. Growth of super molecular structures by crystallization in the brush layer, entangled with molecules of the fiber surface and in the adjoining solution; The formed superstructure can be characterized as "gel-like spherulites";
- d. The crystallized brush layers are subjected to compression which results in compaction of the lamellae onto the fiber surface. Significant transversal orientation of the UHMWPE coating, which is reciprocally entangled with the surface of UHMWPE fibers can be achieved. In this stage we obtain the intermediate-product (prepreg) for manufacture of the composite material;
- e. The final composite material can be manufactured by compression molding or calendering of prepgs to desired shape and properties. A particular advantage is the possibility of attaining orientation of the matrix in different directions.

Realization of processes (a) - (e) is based on our previous investigations on the retardation of dissolution of oriented polymer samples under tension in the suitable solvents or solutions.

Experimental results show that improved interfacial adhesion is achieved in novel composite materials obtained according to this methods.

Session 1B

Transverse Characterization of Interfaces in Continuously-Reinforced SiC/Ti-6Al-4V Composites

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Many proposed applications for continuously-reinforced Ti-based composites require the ability to support transverse stresses. Early efforts to characterize transversely-loaded composites have concluded that the fiber/matrix interface possesses no chemical component to bonding, and that interface separation occurs once the applied load is sufficient to overcome the compressive radial residual stress at the fiber/matrix interface. This residual stress results from the difference in coefficient of thermal expansion between the fiber and the matrix. For composites with a fiber volume fraction of ~30%, interface separation occurs at an applied stress of less than 180 MPa. However, these earlier studies have been conducted on straight-sided samples, where a stress singularity exists at the intersection of the fiber/matrix interface and the sample free surface. The influence of this stress singularity on composite deformation and failure was not accounted for in these previous studies.

Experimental and numerical investigations of the influence of this stress singularity on the mode and progression of failure at the fiber/matrix interface in straight-sided samples will be described. The results of non-destructive observations will be presented to illustrate the progression of interface damage during composite loading. Experimental results obtained on a cruciform-shaped single fiber composite sample, designed to isolate the singularity at the free surface from the point of maximum applied stress, will be presented. The results of these studies show that there is a significant chemical component to interface bonding in SiC/Ti-6Al-4V composites. The magnitude of this chemical bond will be presented for several different fiber coatings. Two competing modes of interface failure under transverse loading, radial tension and tangential shear, will be described.

INTERFACIAL AND PROCESSING ISSUES IN CERAMIC MATRIX COMPOSITES

by

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The development and application of ceramic matrix composites and carbon-carbon systems has been based on toughening mechanisms provided by bridging, deflection, pull out, microcracking and fiber architecture approaches. The mechanical and chemical control of the interfacial bonding and interphase development are based on stability at elevated temperatures with parameteric interfacial control in terms of time, temperature in hostile environments. Micromechanical, thermodynamic and diffusional control models have examined a range of interfacial behavior. The ability to synthesize and control the fiber interface/interphase as well as maintaining ceramic composite coating integrity are based upon thermodynamic stability, lack of degradation and control of the coefficients of thermal expansion. The interface, coating compatibility, processing and interfacial reactions shall be considered for ceramic matrix and selected carbon carbon systems. The interfacial stability can be based environmental protection issues of the composite and fiber coating which serve as interfacial protection layers for high temperature composite systems.

Stability of Copper Segregations on Copper-Carbon Metal Matrix Composite Interfaces under Alloying

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Abstract

The problem of stability of interfaces in metal matrix composites is reduced to the investigation of the segregation of copper atoms at the metal-fiber interface. The calculations of excess thermodynamic functions of interstitial solid solutions is performed. The influence of additives on the stability of copper segregations formed on the fibers is discussed. The wettability of the carbon/copper interfaces is regulated by the solubility of the fiber in the matrix with different dopants. It is shown that the alloying of the matrix by additional element, substituting copper in the interstitial metal-metallocid solid solution changes the value of the mixing energy and influence the volume fraction of two-dimentional segregations of copper. Some additives as the best alloying elements for preventing the copper segregations on the composite interfaces are predicted.

Key words: metal matrix composites, composite interfaces, excess thermodynamic functions, interstitial solid solutions

INTERFACES DEGRADATION OF AN AI / C COMPOSITE MATERIAL UNDER THERMAL CYCLING

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The metal matrix composites are of particular interest to the materials scientist as they retain high strength and stiffness up to temperatures above 300 °C and at the same time they are light weight. There are however problems relating to the chemical compatibility of the matrix and its reinforcing fibers and to the effects of this compatibility upon the durability of the structures made with such materials.

The materials relevant to this study is a symmetric laminated composite with a matrix of a 1050 Aluminium reinforced with 40 % continuous fibers of Carbon. The samples are thermally cycled at different temperature amplitude under increasing values of stresses.

Transverse sections of composites before and after thermal loading have been examined using Scanning Electronic Microscopic and Optical Microscopic analysis. From the micrographs it can be concluded that damage due to thermal cycling without mechanical loading is rather associated with the debonding and the cracking of fiber/matrix interfaces than to the plastic deformation of the matrix and chemical reaction. These degradations, leading to the decrease of the residual mechanical properties, are attributed to the mismatch of the thermal expansions coefficient between fiber and matrix. It is known that chemical reactions occur between carbon fibers and aluminium matrix under thermomechanical loading conditions. To observe the occurrence of chemical reaction products, SEM and Electron Probe Micro-Analysis (EPMA) were performed on composites after 0 and 5000 thermal cycles. All the microstructural investigations undertaken into the interface show no chemical reactions. This can be explained by the bad wetting between carbon fibers and aluminium.

Experimental results, obtained from thermal cycling tests under constant loads, show plastic deformation as the number of thermal cycles increases even at values of stress far below the yield stress. This phenomenon, related to the thermal ratchetting, is then identified to depend on both the applied stress and the magnitude of thermal cycles.

In the design of structure submitted to cyclic loads, the prevention of failure is the most important aspect. In the present case, failure can be related to : the damage fatigue by cracks propagation, to the interfaces degradation by chemical reactions, to the thermal ratchetting which leads to unlimited accumulated deformation or to the interactions of these phenomena.

To identify the main phenomenon leading to the composites failure, Scanning Electronic Microscopic observations have been made on cycled specimens before and after the dissolving of the matrix, and materials have been examined using Optical Microscopic analysis before and after loading at different number of cycles. SEM micrographs show the well developed reaction products on the surface of the fibers.

It may be concluded that, the main phenomenon leading to the failure is the ratchetting for high magnitude of loads and the interface degradation for the low magnitude of loads.

Poster Session 1

INTERFACIAL PHASE SEPARATION IN GLASS-FIBRE-REINFORCED COMPOSITES BASED ON BLENDS OF EPOXY RESIN AND COMMODITY THERMOPLASTICS.

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Thermoplastic polymers are used as a matrix material for various types of fibre reinforced composites, ranging from injection moulded short fibre composites to high-performance structural composites. Historically, thermoplastics have mainly been used in short-fibre reinforced injection-moulding compounds. In the past decade, research has been devoted to the development of continuous fibre reinforced stampable sheet products. Moreover, new developments in thermoplastic composites are aiming on cost-effective high-performance which may attract large-volume markets such as the automotive industry. Since the cost-effectiveness of a product is strongly dependent on raw material costs these developments are mainly focusing on materials like glass fibres as a reinforcement and commodity resins such as polypropylene (PP), polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) as a matrix.

Continuous glass fibre-reinforced composites based on thermoplastic resins are often produced via solution impregnation routes. The solution of the thermoplast in the solvent provides a low viscosity medium which can easily wet the fibres. After impregnation the solvent is removed by drying. However, residual solvent can result in a reduction in T_g and poor interface conditions.

In order to overcome these drawbacks in conventional solution impregnation, a processing route based on the use of reactive solvents is currently under development [1]. In this technique the thermoplast is dissolved in a reactive solvent at elevated temperatures. This thermoplast/reactive solvent mixture is low viscous and consequently fibre impregnation is facilitated. By means of curing the reactive solvent into a non-solvent, phase separation and phase inversion occur. In this way the cured solvent becomes the dispersed phase and a structural part of the thermoplastic material. More important, depending on the chemical properties of the reactive solvent and on the fibre polarity, the reactive solvent can preferentially migrate to and accumulate at the fibre surface during this chemically induced phase separation. In this way an interphase layer forms which can provide a good bonding between fibre and thermoplastic matrix. Because the ultimate mechanical properties of epoxy resins can be varied widely, the properties of this interlayer and therefore the properties of the composite can be controlled.

The development of such epoxy interlayers in glass fibre reinforced composites based on matrix systems such as PP/epoxy and PET/epoxy will be presented. Results will be presented on the relation between composite morphology and composite performance.

MECHANICAL IDENTIFICATION OF INTERPHASE CONDITIONS IN COMPOSITE MATERIALS

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Abstract

To determine the mechanical behaviour of fibre-reinforced composites on a macroscopic scale, a constitutive relation between stresses and strains has to be determined. To define such a relation for a heterogeneous composite material, first the mechanical behaviour of the constituents has to be determined. The interphasial region is often the constituent that governs fracture in transverse or shear loading conditions. Despite their relevance for the performance of composite materials, the mechanical properties of interphases are difficult to determine. Although a lot of work has been done on this subject, mainly in shear loadings, using experiments such as pull-out, microdebond, fragmentation or microindentation experiments, a complete characterization has not yet been achieved. In this study, a coupled numerical-experimental approach is followed. The parameters of the interface, such as the Young's modulus, tensile strength and debonding behaviour are fitted by confronting experimental and numerical results. In the experiments, local strain field distributions are measured in the vicinity of the interphasial region during transverse tensile experiments in a Scanning Electron Microscope (SEM). The strains are measured by placing small dots ($0.2 \mu\text{m}$) on the surface of the specimen, using the electron beam of the SEM. These dots are used as displacement markers. Comparing the coordinates of the markers in reference and deformed configuration gives a displacement field. From these displacements, the strain distribution on the surface of the specimen can be estimated. The experiments are modelled using the finite element method. The geometry of this model is well defined by the position coordinates of the border markers, and the displacements of these markers can be used as kinematic boundary conditions. In this model, the mechanical properties of the glass fibre and the epoxy matrix are known. The parametric identification of the interphase can then be carried out using a sequential minimum variance estimation algorithm. Before fitting the numerical results on the experimental observations, the number of unknown interphase parameters has to be defined. These parameters may include Young's moduli, Poisson ratios or nonlinear functions of material constants. Using a first estimate of these parameters, the displacements of the markers are calculated using the finite element model. The calculated displacements are then compared to the measured displacements, and the difference is used to update the unknown parameters in an iterative procedure. Careful checks on the residual displacements at the final iteration can give information about the validity of the chosen interface model.

THE EFFECT OF ADSORBED MICROSPHERES ON THE MECHANICAL PROPERTIES OF MODEL POLYMER MATRIX COMPOSITES

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Amidine functionalized polystyrene latex microspheres (0.4 μm diameter) have been used as model materials both to simulate the presence of oligomers and other colloidal particles at and to examine the effect of surface roughness on a polymer/fiber interphase. This investigation has been accomplished in two parts, determination of the colloidal adsorption phenomena and measurement of the micro-mechanical properties of a model composite system.

The surface charge phenomena and adsorption behavior of these microspheres at silica surface was studied. Initial experiments involved determining point-of-zero-charge (pzc) of the microspheres and of the silica glass adsorption substrate. It was found that the polystyrene exhibited a pzc of about 9.5. The glass was found to be negatively charged between pH 2 and 10. For these initial experiments, the pH was set to ~5.6. The first variable investigated in the adsorption of the polystyrene microspheres by glass was the time necessary to reach an equilibrium amount adsorbed. The concentration chosen was 160 ppm. It was found that the adsorption density increased linearly for about the first six-eight hours. At this point the rate of adsorption began to slow down and by 12 hours the amount adsorbed had plateaued. Also, the adsorption density was studied as a function of concentration. In this case the amount adsorbed increased linearly through 80 ppm, and kept increasing, but at a lower rate through 320 ppm.

Following the determination of the adsorption phenomena, microbead debonding tests were performed with epoxy microbeads on glass fibers that had been treated under identical conditions to the glass on which the adsorption experiments were performed. The treated fibers were examined both before and after debonding by scanning electron microscopy. It is expected that the amidine functional group at the surface of the microspheres can bond with the epoxy polymer, so that the microspheres can act as coupling agents. Initial debonding experiments indicated that adsorption of the microspheres increased the interfacial shear strength by 50%. Future experiments include simultaneous adsorption of γ -APS and microspheres to further enhance the shear strength of the interphase.

A Simple Fracture Mechanics Method for Measuring the Interfacial Toughness with Microbond Tests

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ABSTRACT

We derived a simple energy release rate analysis for the microbond specimen that includes energy released due to thermal stresses. By assuming that the droplet debonds from the fiber when the energy released from interfacial crack growth exceeds the fracture toughness of the interface, we predicted debond force as a function of droplet length and diameter. This fracture mechanics model of the microbond specimens agrees better with experimental results than the commonly used average shear stress failure criterion.

FIBRE FRAGMENTATION TEST WITH POLYETHYLENE COMPOSITES

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ABSTRACT

Ultra high molecular weight polyethylene (UHMW-PE) fibres exhibit a high specific strength and stiffness combined with a high strain to failure. They especially improve the damage tolerance, fatigue and impact resistance and vibration damping when used as reinforcement in thermoplastic matrices.

Polyethylene as a matrix is chemical resistant to most solvents, has a low coefficient of friction, is biocompatible and hydrophobe. It is therefore widely used for biomedical application, as in artificial hips or knee-joints. A PE-fibre/PE-matrix composite would not only improve the properties of bulk PE, it would also enable to have a fully recyclable composite.

Both LDPE and HDPE have a lower melting temperature than UHMW-PE fibres. They can potentially be used as matrices in a PE/PE-composite. However the major problem in using PE fibres is the poor interfacial bonding because of the chemical inertness of the fibres.

The object of this study is a qualitative analysis of the interfacial shear strength between PE fibres and PE matrix based on fibre fragmentation tests. Dyneema SK65 fibres from DSM are used in this study. The matrix was commercial HDPE. The specimens were manufactured by film-stacking in a heated laboratory press. The morphologies were varied by two different cooling rates. The morphology of the matrix was documented by light micrographs. Slowly cooled specimen showed a coarse spherulitic matrix and a transcrystalline area around the fibre. In the case of high cooling rates, which means quenching, the spherulites were much smaller and there wasn't any transcrystallinity.

Quenching results in a 17% higher number of breaks per specimen in the fragmentation test than slowly cooling (Figure 1). This means that the interfacial shear strength increased about 17% with the higher cooling rate. SEM investigations of the fibres after the fragmentation test showed that they fibrillated at its end and that there are kinkbands on the fibre surface. We concluded that the fibres failed after the breaks in a compression after tension mode. With the SEM micrographs taken from the surfaces of the broken fibres it can be demonstrated that debonding takes place in the low molecular skin of the fibres. Which indicates that the low molecular skin is the weakest point of the fibre matrix interphase.

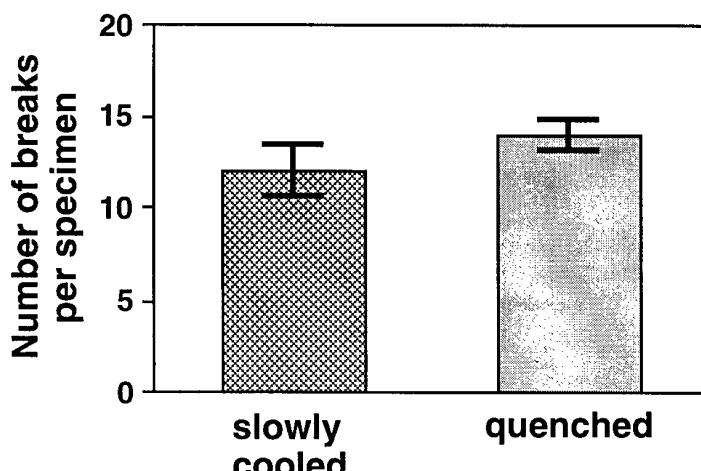


Figure 1: Number of fibre breaks per specimen in the fragmentation test

MORPHOLOGICAL CONTROL IN BARIUM SULPHATE FILLED POLYPROPYLENE/POLY(STYRENE-CO-ACRYLONITRILE) BLENDS

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Multicomponent thermoplastic blends have become increasingly important because of the possibilities to design mechanical properties in a controlled way. One alternative in this broad spectrum is to mix a rubbery material in a polyolefin matrix in addition with a filler [1-2]. An important question concerning the structure of these materials and thereby their properties, is how and in which phase the filler is dispersed. This depends on the chemical character and interaction between the filler and the polymers, as well as the mixing technology, process conditions and volume shares.

A filled thermoplastic blend consisting of polypropylene, poly(styren-co-acrylonitrile) and barium sulphate is used to investigate and confirm that it is viable to control the polymer phase in which the filler is occluded as a function of filler size and concentration of added dicarboxylic acid-grafted low molecular weight polypropylene (PP-g-MAH). The morphology was analysed using SEM and was further correlated with dynamic mechanical measurements.

The occlusion of the filler in the SAN phase in the case without the addition of PP-g-MAH must be a result of preferential interaction between the acidic SAN and the barium sulphate filler, this relationship is altered with the addition of PP-g-MAH. A high enough concentration of the acidic PP-g-MAH results in the dispersion of the filler in the PP/PP-g-MAH phase.

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THE INFLUENCE OF THE CURING PROCESS
ON THE CRAZING LEVEL OF FILAMENT WOUND LAMINATES

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The problem of manufacturing a cylindrical water softening pressure vessel made of semi-transparent glass fibers/polyester by filament winding is discussed. The required test pressure is 15 bar, and the required level of transparency is such that it is possible to identify a change in the color of the softening material inside the vessel when looking through the wall from the outside. An important consideration is that neither the pressure testing nor repeated exposure to working pressure cycles should degrade the level of transparency.

Because the level of transparency of the cylinder's wall thickness (as thickness increases, transparency decreases), designing the wound layers must be optimized to achieve minimum cylinder wall thickness. However, there are two limiting factors which inhibit this optimization:

- There must be a safety factor of 2 (i.e. 30 bar minimum burst pressure).
- The cylindrical stresses during pressure tests and working pressure cycling must be lower than the crazing stresses in every wound layer to maintain the required level of transparency.

The parameters which may be varied to achieve the optimization are: the number of hoop layers, the number of helical wound layers, and the winding angle of the helical layers.

It was shown that, for a given cylindrical pressure vessel having a constant wall thickness, decreasing the winding angle results in an increase in burst pressure. On the other hand, it was found that increasing the winding angle reduces the crazing stresses. Such phenomena are explained by the great differences between polyester and fiberglass linear expansion coefficients such that, after curing, there are residual tensile stresses in the hoop layers which increase as the winding angle decreases. These residual stresses, together with the stresses induced by the test pressure, may sometimes be greater than the crazing stresses - an incorrect design.

Several conclusions, based on experimental data and confirmed by numerical analyses, may be formulated:

- The addition of hoop layers or helical layers to vessel laminate does not essentially improve an incorrect design.
- The effective means of transforming the incorrect design into a correct one is by increasing the winding angle of the helical layers.

**CALCULATION OF THE NEW DIMENSIONLESS
POLYMER ADHESION-SENSITIVE PARAMETERS
BY CHARACTERISTICS OF THE RESPECTIVE MONOMERS**

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The adhesives is under the influence of two contrary forces. First of these forces is further to spreading and can be approximate the surface energy, σ . The second force is aspire to tighten the liquid adhesive in the drop, and can be approximate the cohesion energy of repeating units, E_c . In the first approaching the complex parameter ratio $\alpha = E_c/\sigma$. But it is not dimensionless (though it justly takes account of regularities for change in the strength of adhesive joints, P), so it is suggested to change for characterizing constant

$$\alpha' = k \delta^4 E_c / N_A \sigma^3, \quad (1)$$

where $k = 0.1205$ through change in dimensions of all variables into SI system, δ is solubility parameter, and N_A is Avogadro number obtained by the 2nd π -theorem of similarity theory. To observe the unity of approach to calculation of adhesion-sensitive parameters, ASP, we express α' value in the terms of function of refractive index, n_D , and refraction, R , of the resrespective monomers. Then

$$\alpha' = (k'/\delta) \{[\rho_m R_m (n_D^2 + 2)]/[M(n_D^2 - 1)]\}^{1/2}, \quad (2)$$

where $k' = k c_o A^7$; M , c_o and ρ_m are molecular weight, packing coefficient and density of monomers accordingly; A is the constant of Hildebrand's equation. For further improvement of this approach it would appear reasonable to take into account mentioned above the regularities and apart from surface and cohesion energies of monomers, account must be taken of the flexibility of their macromolecular chains, s , as ratio of cohesion energies of repeating unit and segment, E_s . To do this, we enter simple function of not dimensionless characteristics using the form of initial expression

$$\alpha'' = \alpha' s. \quad (3)$$

After substitutions (including of polymer density) it takes the criteria form:

$$\alpha'' = k'' \{(\rho_p E_s) / (M^{7/2} \delta^3)\} \{[\rho_m R_m (n_D^2 + 2)] / [n_D^2 - 1]\}^{5/2}, \quad (4)$$

where $k'' = k' A^7 N_A^{-1} = 2288.92$. However, taking into account nonintegrality of indicator of degree in the ratio $\delta = [E_c / (N_A V)]^{1/2}$, the last product is reasonably replaced by characterizing relation

$$\alpha'' = \alpha' s^{1/2}. \quad (5)$$

(V is Van der Waals' volume). The simple substitutions are leads to final Equation $\alpha'' = k''' (\rho_p / M) |V / (C^5 E_s)|^{1/2}, \quad (6)$

where $C = (3.4577 - 0.9877 \eta^{1/8}) / (20.3859 - 3.4048 \ln \eta)^{1/3}$; $k''' = k'' N_A^{3/2} = 1069.90$; η is dynamic viscosity of monomer. The complex dimensionless ASP are calculated for 31 α -cyanoacrylate adhesives. The quantitative relationships between the calculated ASP of all monomers and the adhesion strength of their adhesive joints with 5 metals have been found. The functions $P(\alpha'')$ are discussed. An analysis of P_{calc} values confirms the validity of the approach developed of calculation of adhesion-sensitive parameters.

THE EFFECT OF ADHESION PROMOTER LAYER THICKNESS ON THE
ADHESION STRENGTH BETWEEN SILICONE RUBBER AND ALUMINUM

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ABSTRACT

The dependence of adhesion strength on the thickness of adhesive layer between two adherents is a well known fact. Adhesion promoters (coupling agents, primers) between unlike materials however, cannot be regarded simply as adhesives. They form an interphase with characteristic substructure, rather than a monomolecular layer. In this contribution we have tried to explore the effect of the thickness of this interphase on the adhesion strength between aluminum and a liquid silicone rubber.

First the adhesion promoter solution has been applied to the surface of silicone wafers of extreme smoothness by spin coating, the solvent was evaporated and the primer was cured. Then the thickness of the cured layer has been determined by ellipsometry and by mechanical means (step height measurement by needle contact). Both methods yielded similar thickness data if both methods could be applied. Usually ellipsometry could be used with thinner, the mechanical method with thicker layers. The layer thickness was measured at different spin rates and primer concentrations and a calibration curve was fitted to the data.

Using this calibration curve adhesion promoter layers of different thickness have been applied to discs made from rolled aluminum sheets. Addition curing silicone liquid rubber layers were cast on the primed aluminum substrates and the adhesion strength was determined by a special peeling test. In spite of the scattering of the data the qualitative behavior was quite clear: in the 45 - 250 nm thickness interval the adhesion strength increases. Multiple layers or brush coated layers are laterally inhomogeneous and result in inferior adhesion strength.

LOW FREQUENCY ACOUSTIC SCAN ANALYSIS OF MORPHOLOGY MODIFICATIONS OF VINYLESTER RESINS NEAR A SURFACE

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In a previous study [1], infrared spectroscopy and ¹³C-NMR analysis have clearly revealed the existence of a thick interphase in vinylester resin cured in contact with different materials, whatever their nature (glass, aluminium, ...) or geometry (plates, fibres). Such an interfacial layer stems from the variation of the relative concentrations of polystyrene and vinylester polymer from the interface to the bulk, certainly due to the migration of styrene molecules towards the bulk specimen during curing. The extent of this modification is large since the thickness of the resulting interphase is ranging from about 150 to 300 μm . Preliminary mechanical measurements, performed on thin sections (15 μm thick), have shown that a gradient of the elastic modulus certainly exists in this interphase. Such a phenomenon could strongly affect the magnitude of the stress transfer from the matrix to the fibre in composite materials and, then, their final performance. The aim of the present study is to analyse more deeply the elastic modulus gradient in that type of interphases by means of an acoustic scan method at low frequency (typically 15 to 25 MHz). With this technique, the specimen, totally immersed into water, is subjected to an incident beam and the acoustic energy reflected by the solid/water interface is analysed. This quantity is directly related to the density, the elastic modulus and Poisson coefficient of the specimen and, therefore, an evolution profile of these characteristics can be obtained by scanning. Since the presence of an interphase in our case is due to the variation of the polystyrene relative concentration near the surface, crosslinked networks of vinylester resin obtained by reaction of the prepolymer with different contents of styrene monomer, ranging from about 35 to 60% w/w, are first analysed. To a first approximation, their acoustic reflectivity decreases linearly with the styrene content. Knowing the elastic modulus of these networks, it is therefore possible to determine the structural and mechanical evolution profiles of interphases created *in situ* in vinylester resins. For example, in a specimen crosslinked with 40 % w/w of styrene, a continuous decrease of the acoustic reflectivity is observed from the surface to the bulk, indicating that the styrene content and the elastic modulus do not exceed 15 % and 1 GPa near the surface, instead of 40% and about 3.5 GPa in the bulk, respectively. All the results obtained in this study are in good agreement with previous analyses and confirm clearly that the acoustic scan method is a good tool for analysing structural modifications in polymer materials.

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INTERFACIAL STUDY IN PITCH-BASED CARBON FIBRE / POLYCARBONATE MODEL COMPOSITES

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The aim of the present study is to correlate the micromechanical behaviour of fibre-polymer interfaces to their thermodynamical properties, i.e. to the strength of physico-chemical interactions established between the fibre and the matrix. Single fibre composites constituted by high or ultra-high modulus pitch-based carbon fibres and polycarbonate matrix (Makrolon, Bayer) are analysed. Different types of fibres were used : P75S (a commercial and sized fibre, elastic modulus $E_f = 520$ GPa) and P120J ($E_f = 830$ GPa) from Amoco Performance Products, as well as Ar-mesophase ribbon shaped carbon fibres ($E_f = 850$ GPa) produced at Clemson University [1]. The P120 and ribbon fibres, initially untreated and unsized, were subjected to different oxygen plasma treatments. The fibre surface was analysed by scanning electron microscopy, X-ray photoelectron spectroscopy and wettability techniques, in particular dynamic contact angle measurements, allowing us to determine its surface energy components. The mechanical properties of interfaces were assessed by means of a tensile fragmentation test on single fibre composites, leading to the calculation of a mean interfacial shear strength from a purely elastic stress transfer analysis [2]. First, before fragmentation, polarised light microscopy examination of the compression moulded composites show the presence of a regular stress pattern along the fibre-matrix interface, bright spots being observed at fixed distance for each type of fibre. Such a pattern is due to residual thermal stresses that are non-homogeneously distributed along the interface. The average distance between bright spots is clearly dependent on the fibre surface energy and correlates well with the critical fragment length determined by fragmentation test. Secondly, it can be observed that the interfacial shear strength increases linearly with the "polar" component of the surface energy of the fibre, in rather good agreement with previous analyses on other systems [3]. However, for ribbon shaped fibres, which exhibit an elliptical cross section with an axes ratio of about 3.2, the interfacial shear strength is considerably higher (approximately 4 times) than those obtained for circular fibres. Such a result seems to indicate that the classical stress transfer analysis, based on Cox' approach [2], cannot longer be valid when the shape of the fibre is different from a cylinder.

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ESTIMATION OF MICRACKING AT THE INTERFACES
BY X-RAY DETERMINATION OF THE STRAINS IN COMPOSITES

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The difference between compression of the phases during composite firing and cooling gives rise to stress at the interface. These stresses can exceed the strength of the phases or their bonding and cause micro-cracking reducing the material strength. Stress relaxation due to such cracking is proportional to concentration of the interface ruptures and can be used for their quantitative estimation.

The stress relaxation degree P was determined by the comparison of the theoretical microstrains ϵ_c calculated for ideal phase bonding and experimental ones ϵ_{ex} : $P = (\epsilon_c - \epsilon_{ex})/\epsilon_c$. The calculated strains are $\epsilon_c = (\alpha_p - \alpha_m) \cdot (T_1 - T_0)$ where α_p and α_m are the thermal expansion coefficients for the studied phase and composite respectively, T_1 is a temperature of composite transition into unstressed viscous-elastic state, T_0 is an ambient temperature. The experimental strains were measured based on line shift on the X-Ray diffraction pattern.

This method was used for estimation of the interface microcracking in the model glass/crystal composites with the different contents of the phases and different filler grain size (quartz/borosilicate glass, zircon/borosilicate glass systems); the different thermal expansion coefficients of the glass matrices (rutile/glass systems) as well as in the glass-ceramics containing α - cordierite, β - spodumene and β - eucryptite.

The increase in the stress relaxation degree due to the growth of the grain size or due to the rise of the initial stresses at the interfaces was found, being in good agreement with the theory. Linear decrease of the composite strength proportional to the increase of the stress relaxation P was observed for the studied glass/crystal pairs.

Experimental results showed that proposed simple X-Ray method can be useful for the estimation of interface debonding and its relation to the strength of other composite systems.

HIGH-STRENGTH AND DURABLE GLASS FIBRE REINFORCED CEMENT

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Low corrosion resistance and adhesion strength of glass fibre (GF) in cement stone (CS) are the main obstacles on the wide use of GF reinforced cement. The new type of low cost GF, inert to cement pH and possessing high bending strength, is being developed by H.G. Hodglass Ltd, Israel.

The effect of interface bond strength in GF-Binder-CS composites on their mechanical properties and durability was studied depending on the types and content of the binders, coupling agents and cements as well as CS hardening mechanism.

Cements of two hardening types were used for testing: hydration hardening (Portland cement, alumina cement) and acidic-basic hardening (magnesia cement). For the estimation of the reinforcement adhesion and durability "Hodglass" GF was introduced directly into hardening cement paste, using 40x40x160 mm bars and 140x140x3 (6, 10) mm plates. GF tensile strength was determined after 6 months storage in aggressive liquid of the composition corresponding to the liquid phase of the hardening Portland cement. Kinetics of CaO absorption by the GF of different compositions were studied in order to define new compounds (phases) in the contact area for CS-GF system.

The experimental results showed that the strength of CS reinforced with the "Hodglass" GF increases regardless of CS hardening mechanism. Bending, compression and tensile strengths were increased several fold and achieved for the optimal composites to 100, 450, and 60 MPa correspondingly. The kinetics of CaO absorption by the GF remained practically unchanged after storage in aggressive liquids. This fact along with the strength increase allows to conclude that "Hodglass" GF is a stable reinforcement in the hardening CS.

At the same time adhesion strength of GF with CS as well as GF reinforced cement strength depend on the cement hardening type and structure, on the type and content of the coupling agents, and reinforcing mode. Combination of these factors for the interface control was established.

The physical model of interface bond strengthening in GF reinforced cement is discussed.

The obtained data show the possibility of fabricating of high-strength and sufficiently durable composites based on different cement matrices and "Hodglass" GF filler. These composites are promising to be used for the production of the thin-wall units.

EFFECT OF THE CHAIN LENGTH OF COUPLING AGENTS ON THE SILICA-POLYETHYLENE ADHESION

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It is well known that adhesion and mechanical properties of filled polymers can be greatly improved by addition of appropriate silane coupling agents. This work deals with mobility and conformations of chains at the interface of polyethylene / glass fiber composite.

In a first time, monofunctional organosilanes, as $\text{CH}_3(\text{CH}_2)_n\text{Si}(\text{CH}_3)_2\text{Cl}$ with n varying from 3 to 29 are deposited on oxydized silicon wafers and on nanometric silica. Two methods for silanization are considered: adsorption from solution (denoted Sagiv process) and silane surface condensation (denoted Kovats process). Contact angle measurements are used to characterize grafting and to acquire information on the organization of alkyl chains. ^{29}Si NMR CP/MAS allows to follow the silanization reaction and to show the covalently coupling between silanes and silica.

The grafting process has a great influence on the formed monolayers. By considering the wetting hysteresis, we can evidence that silane monolayers adsorbed from solution are less well-ordered than those of Kovats films. However, after an UV cleaning, the two methods become similar. Ellipsometry measurements and AFM microscopy confirm the previous conclusions and give informations about the structure of the prepared monolayers.

The study of this model system allows us to approach the grafting of longer chains such silane functionalized polyethylenes. Oligomers with different molecular weight have been synthesized by platinum catalyzed hydrosilylation reaction with dimethylchlorosilane of an hexene-polyethylene copolymer containing unsaturated bonds.

Polyethylene / silica adhesion is evaluated in terms of fracture toughness of the interface using an asymmetric double cantilever beam testing geometry. This test, developped by Brown, is shown to overcome many of the traditional problems of adhesion measurements, such as failure away from the interface and effects of far-field deformation in the polymer.

The influence of the alkyl length of silanes on adhesion fiber/matrix is studied. We expect more adhesion if the grafted chains interdigitate with the matrix, i.e in the case of grafted silanized polyethylene chains. The interdiffusion of grafted chains, the grafting density and the chain length are important parameters. The cocrystallisation with the polyethylene matrix is also considered.

SAWDUST SURFACE MODIFICATION

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Lignocellulosic fillers (e.g. sawdust) are used as polymer reinforcement, mainly because their low cost, their availability and renewability. Besides natural fibers have low density with good resistance to breakage during processing.

A major limitation in their commercial use is the incompatibility with non-polar polymers (e.g unsaturated polyester). This problem can be solved with an appropriate fiber surface treatment.

Sawdust from a local species (Eucaliptus Saligna) is characterized: particle size, particle size distribution and moisture content. Small particles (less than 57 μm) are selected to be compatibilized to a commercial unsaturated polyester. Filler specific area is determined by adsorption technique (BET), and maleic anhydride (MAN) is used as surface modifier. Water retention values (WRV) are determined for different concentrations of MAN in order to verify the efficiency of chemical treatment a good fit of the experimental results is obtained using the Langmuir equation for adsorption.

Dynamic mechanical analysis allows to establish an important effect of humidity and sawdust content on the composite properties, however, no significant effect of the chemical treatment has been found. This is probably due to the very low value of specific area of treated and untreated sawdust (2 gr/ cm^3).

A further treatment of smallest particles with an alkaline solution (NaOH, 0.1N) gives a BET specific area of 9.5 g/cm^3 , approximately four times greater than the original sawdust, resulting in better conditions for studying the further modification with MAN.

**Al₂O₃-ZrO₂ COMPOSITE COATINGS FOR
THERMAL BARRIER APPLICATIONS**

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ABSTRACT

Graded alternate layers(upto six, 75 microns each) of Al₂O₃ and 8%Y₂O₃-ZrO₂ and their admixtures(150-450 microns) were plasma sprayed on bond coated (NiAl, 100 microns) mild steel. They were evaluated for thermal shock resistance (between 1273⁰K and 298⁰K), thermal barrier (temperature drop across the coating for hot zone temperature ranging from 1073 to 1373⁰K), hot corrosion resistance (molten NaCl corrodant) and depth of attack (microscopy /EDXA), adhesion strength and phases (XRD). While temperature drop of 423 - 623⁰K were observed, the coatings were well adherent even after 100 up and down thermal shock cycles. In the sequence of the graded layers , the oxide which is directly in contact with the bond coat appears to influence the properties especially in the 150 and 300 microns thick coatings. Failure occurs at the interface between the bond coat and the substrate due to the formation of a pile- up layer consisting of Fe-Zr-Al-O compound and also due to the poor thermal shock resistance of Al₂O₃ coatings when directly exposed to high temperature (1273⁰K). Molten NaCl attacks the films easily at high hot face temperatures (1273⁰K for 1 hour) and a significant drop (50 - 60%) was obtained in the adhesive strength. Diffusion of alkaline element is also found to depend on the chemical composition of the overcoat directly facing the molten corrodant.

An electrochemical study on the behaviour of the metal-metalloid glass (Fe,Cr)₈₀(P,C,Sn)₂₀ in aqueous solutions containing chloride ions

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Abstract

Metallic glass combines excellent mechanical and magnetic properties with a high resistance against corrosive aqueous solutions. Because of its extended stability in the alkaline environment one of the many applications of this material is given by composites such as glass fibre reinforced cement and concrete (GRC). Contrary to composites with a steel reinforcement [1] there are no corrosion problems initiated by chloride ions of the cementitious matrix or by chloride ion permeability of mortar if the metal-metalloid glass fibres are used. But the interface and its roles in GRC have not yet been enlightened completely.

Properties of the metal-metalloid glass (Fe,Cr)₈₀(P,C,Sn)₂₀ were studied according to [2]. The behaviour of the glass was investigated by means of an electrochemical method (potentiodynamic technique). In the measuring system the glassy ribbons were used as rotating electrodes immersed in aqueous systems containing chloride ions. Current-potential curves were measured for solutions with the varied parameters as pH-value, temperature and the chloride ion concentration. These factors affect and determine the interfacial bonding strength between a cementitious matrix and a reinforcing glassy material in different ways which are discussed in this paper.

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METALLIZING NON CONDUCTIVE SURFACE BY RF PLASMA TECHNOLOGY

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Several processes are currently used to metallize non conductive materials. Some of these processes allow to produce devices with high surface conductivity or items showing attractive surface properties from an aesthetic point of view. The technology employed, however, leads to materials showing very poor adhesion between coating and substrate. In addition the non conductive materials needs a surface pretreatmens that is highly polluting.

Cold plasma treatment is a powerful technique to improve surface properties and if plasma is generated in the range of radio frequency domain, it can be said a "very clean" technique. Cold plasma is a useful technique to obtain organic or inorganic thin films. Many researcher devoted their study to investigate the properties of coatings obtained by Plasma Enhanced Chemical Vapour Deposition (PECVD). On the other hand a considerable effort was devoted to investigate deposition of metallic film on a non conductive substrate by sputtering of a proper target.

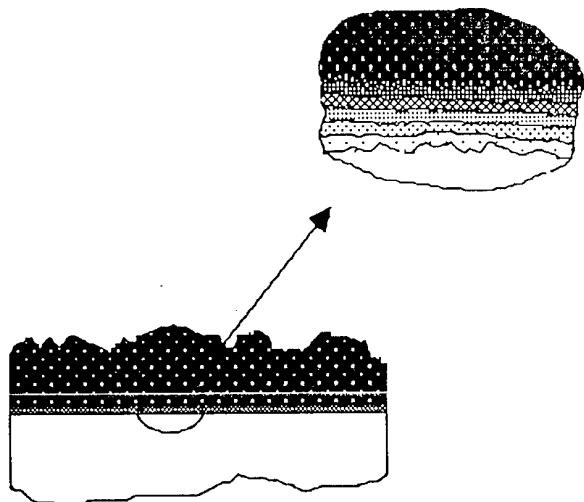


Fig. 1. Schematic of metal graded coating.
metal filled coating.

The tentative study performed in this work shows the possibility to metallize materials like "Teflon" or silicon via RF plasma treatment. Materials used in this study were Cu, W, Au as sputtered metals. The coatings were realised using several gases to deposit films containing Si, C, O, H or C, F, O, H.

Results obtained from experimental data have shown that it is possible to obtain a graded metal containing thin film via co-deposition of metals from sputtering process and organic coating from PECVD.

Aim of this work is to investigate the realisation of an organic or inorganic metal filled thin film, obtained via contemporaneous PECVD and sputtering of metal.

Metal is present in coating as clusters sputtered from a proper metal target, the matrix could be a organic or inorganic material deposited during the sputtering process.

The amount of metal may be variable in the film thickness (see fig. 1).

Furthermore, by changing the process parameters, during the deposition of film, it is possible to realise a graded

Fine-scale processes on the interface of plastic fibre and polymer matrix

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This work presents the results of experimental and mathematical simulation of plastic deformation process of metal fibre in elastic polymer matrix.

The experimental simulation of deformation process of plastic fibre in elastic matrix has shown the availability of neck set formation mechanism on the fibre in conditions of large deformations.

Theoretical research conducts the mathematical simulation of process of formation and stabilization of the neck. The special attention is paid to numerical simulation of interfacial adhesion.

On the base of the received results the model of neck set formation mechanism on the fibre is developed.

The present work are carried out at support of Russian Fund of Fundamental Researches.

Theme: 4. Interfacial Adhesion: Theory and Applications.

THE EFFECT OF LOADING IN LIQUIDS ON THE ADHESIVE STRENGTH OF FIBER-POLYMER SYSTEMS.

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Fiber-polymer joints are used for investigations by many groups of research workers in various countries. The efforts of these groups have been focused on the study of the effect of various factors on interfacial strength, factors that operate during the fabrication, storage and testing of joints, primarily the nature of fiber, treatment of the fiber surface, the structure and composition of the polymer adhesive, the conditions under which the joints are prepared and the shape and size of specimens.

The behaviour of joints upon loading in liquid media has not been studied at all. Meanwhile, it is interesting to examine such behaviour from both a theoretical and a practical point of view. The presence of liquid molecules can alter the kinetics of origination and growth of defects responsible for the fracture of the interface. Accordingly, the fracture mechanism and adhesive strength can also be changed.

The purpose of this work is to study experimentally the effect of the surrounding liquid on the strength of interface of polymer - solid joints.

The shear adhesive strength τ of fiber - polymer joints was tested by the pull - out technique at the temperature 20°C. The typical representatives of thermosetting network and linear thermostable polymers - the epoxide composition EDT-10 (based on DGEBA) and poly(arylene sulphone) PSK-1 were used as adhesives; the carbon fibers and a steel wire were used as a substrate. Loading was made in water and in alcohol (i.e., in liquids with substantially different values of surface tension) and also in air. For measurements was used the adhesion tester which was developed in the Institute of Chemical Physics and which makes possible the testing of specimens in various liquid and gaseous media. It was found that upon loading in liquids the values of adhesion strength either retain the same (for fiber - PSK-1 joints) or decrease (for fiber - EDT-10 joints). The extent of decrease depends primarily on the nature of adhesive and of the specimen size. The nature of fibers and surrounding liquids change the boundary strength in a lesser extent.

This work is supported by International Science Foundation.

MORPHOLOGY OF POLYURETHANE GRAFTS AND BLENDS

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The object of this study was the observation of morphology with electron microscopy and the exploration of the dynamic mechanical properties of polyurethane grafted onto styrene-styrene sulfonic acid copolymers and the blend of polyurethane with the same lightly sulfonated polystyrene.

Dynamic mechanical studies showed, that the ionic interaction between the sulfonic anions on styrene and the different cations (allophanate, urethane and tertiary nitrogen) on the polyurethane enhanced miscibility of the blend.

In the grafts the cation was located only on the tertiary amine (of N-methyl diethanolamine used as the chain extender of polyurethane), because a procedure was employed that involves stepwise grafting onto sulfonated polystyrene of N-methyldiethanolamine follows by chain growth on the hydroxyl sites of polyurethane structures of interest.

In mechanical tests the one glass transition temperature is observed for the grafts and blend with the shortest soft segment ($M_w \approx 400$) of polyurethane. Phase separation occurs when the soft segment exceed a certain length ($M_w > 725$) and the alloys of polyurethane and sulfonated polystyrene obtained by the grafting method yield materials in which the phase purity in phase-separated systems seems to be better than in the regular blend of similar composition.

But on the electron microscope pictures we can observe very subtle domain structure even in the case of short length of soft segment of polyurethane in both alloys. It means that we do not obtain the real miscibility on nanometer scale even in the presence of ionic interactions between two investigated polymers

A MONGREL FINITE ELEMENT APPROACH FOR INTERLAMINAR STRESSES DETERMINATION IN MULTILAYERS COMPOSITE LAMINATES

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The prediction of damaging modes and associated strength of multilayers composite laminates needs the correct knowledge of the local stresses near possible crack tips, near free edges of the structure and at different interfaces between layers. Experimental determination of these stresses requires unfortunately highly expensive procedures and technologies, so that numerous numerical tools, especially finite elements, have been developed in order to reduce these costs. Nowadays, experimental approaches are more and more strictly reserved to validate mathematical models.

Usually, the most frequent damaging mode in composite laminates matches with the debonding of two adjacent layers. This phenomena, called delamination, begins with the cracking of the interlaminar matrix and leads to a complex problem in which geometrical and material discontinuities and coupled fracture modes are involved.

The stress gradient near a delamination crack tip is very sharp and leads to infinity (stress singularity) while oscillating, so that a satisfactory approximation by classical finite elements needs very refined and expensive meshes. This singularity is governed as well by the exponent of singularity δ as by the stress intensity factors K_i .

The first step of this work consists in sensitiveness tests of studied materials geometrical and physical properties on the order of singularity δ . We show that several parameters may have a strong influence on singularity orders - and therefore on stresses - as well for delamination, free edges and general crack configurations.

The second step aims at the computing of a new class of finite elements allowing to catch efficiently and economically the stress field in the vicinity of a delamination crack tip and the interface stresses realizing the local interfacial equilibrium : the double singularity mongrel hybrid finite element. The classical displacement-formulated finite element approach doesn't allow to determine exactly and easily the stresses at a singular point as at a delamination crack tip. Comparatively, the stiffness matrix and the loading vector of the mongrel finite element is formulated on the basis of a special variational functional with two fields $\Pi(\underline{\sigma}, \underline{u})$. The displacement vector \underline{u} is defined over the element boundary and univoquely extended inside the element as internal equilibrium is verified. Moreover, the stress field is only defined and in equilibrium inside the element and is constituted by singular and regular parts containing the Lekhnitskii's laminate elasticity solution. The singular stresses contains the main term of the asymptotic development of the solution near the crack tip.

Finally, the last step consists in the interface stresses and stress intensity factors computing. It is shown that the twisting shear mode is the most dominant one and that the interlaminar response has a tridimensionnal form until specific angles. Two numerical examples have been treated in order to prove efficacy of this new and powerful finite element class.

Development of a surface topography on the metal-metalloid glass (Fe,Cr)80(P,C, Si)20 by an oxidative treatment and formation of a cement-reactive surface layer investigated by REM/EDXA

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Abstract

High performance glass fibre-reinforced concrete (GRC) prepared from Ordinary Portland cement (OPC), various supplementary cementitious materials and fibres are increasingly finding their use in construction worldwide. Adhesion at the reinforcing fibre/inorganic polymer matrix interface is one of the most important parameters determining the performance of such a composite material. Since the fibres and matrices are usually chemically different, strong adhesion at their interfaces is needed for an effectiv transfer of stress and load distribution through an interface [1]. For silicate glass containing composites the interface has strongly an influence on micromechanical properties of this material [2].

The (Fe,Cr)80(P,C, Si)20 ribbons are inert in an aqueous alkaline solution of a pH = 14 [3]. Initiated by the study of corrosion in the steel/Ca(OH)₂ + Cl⁻ system [4] an oxygen supply was applied to influence interfacial properties by formation of a cement-reactive layer on the glass surface.

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DISCRETE MODELS OF FAILURE FOR PARTICULATE RUBBER COMPOSITES

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A stochastic discrete model is offered which simulates the behavior of particulate composites capable to generate and accumulate scattered structural microdamages and the final break-down of the model system. Its basic geometry involves a number of cross-sections in tandem each containing a number of structural elements (links) connected in parallel. This construction can simulate not only the microdamage appearance and accumulation but also the macrofailure occurrence. During extension, the damage accumulation enhances the macroscale elastic nonuniformity and finally leads to the loss of longitudinal elastic stability of the specimen. The latter provides failure manifesting itself as the instantaneous disruption of all the links in the one most compliant part of the body. This kind of modeling, elucidating the microstructural processes, gives notion how the fracture develops, the recourse to arbitrary fracture criteria being not needed.

The importance of the hierarchical approach in describing composite properties is demonstrated. The interplay of the cross-section current rigidities is shown to be the main factor controlling the failure conditions. Hence, the cross-sections are shown to be very important mesolevel elements lying between the basic microscopic elements (links) and macroscopic dimensions of the body. A good prediction of failure seems to be hardly possible, if the characteristic cross-section behaviour is ignored.

The simple model version not only reflects qualitative features of the failure phenomenon, but also provides some important quantitative results that could hardly be predicted in advance. It demonstrates how the critical degree of damage and the critical longitudinal elastic nonhomogeneity depend on the length and uniformity of the composite specimens. It implies that unbounded increase in the length of specimens in no case can reduce deformations and stresses to zero. The scatter of the specimens ultimate stresses and strains in repeated numerical experiments can be calculated and used for approximate estimation of safety factors.

An advanced model takes into account a set of the refining factors for structural elements, such as filler volume content; moduli for bonded and debonded cell; adhesive debond strain; matrix breaking strain. It describes well the experimental data with plateaus on tensile curves characteristic of highly filled rubber composites. The offered numerical experimentation based on this model enables one to gain deeper insight into the hidden structural reorganization causing the observed macroscopic tensile and failure behaviour.

The simulation procedure offered allows one to perform further refinement, no basic reconstruction of the model backgrounds being needed.

This work was supported by grant N 94-01-00465a RFFI.

About estimation of adhesive bond strength.

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In the most experimental tests exploited to estimate the adhesive strength only two parameters are measured directly: the breaking load F and the surface (contact area) S of joints. The quantity F/S is usually called an adhesive strength σ . However, as it is well-established, this quantity depends strongly on the shape and the size of the joints. Thus, the value of adhesive strength determined as mentioned above is a conditional quantity. Their dependence on the joint geometry (on scale factor) is associated with non-uniform distribution of both internal (residual) and external stresses acting at the interface. Residual stresses arise during the formation of a joint and upon its subsequent cool-down. They exist in a joint prior to its testing.

The non-uniform of stress distribution complicates significantly the interpretation of experimental results. The questions arise: what areas of contact should be used to compare adhesion of different systems or single system under different test condition? What does the adhesive strength measured in experiments characterise? But the main question is: what is the measure of adhesive strength?

The traditional method of overcoming of scale effect problems in technical applications is the strict specification of test conditions. However for theoretical considerations of the adhesive bond strength problems such standards are not suitable. In order to discuss the mechanisms of interaction at the interface it is necessary to know the "true" value of adhesive strength, i. e. the value that is a characteristic of a given pair and is independent on the size and the shape of specimens.

Since the non-uniformity of stresses is insignificant only with a small adhesive joint area the true value of adhesive strength can be determined as $\sigma = \lim_{S \rightarrow 0} (F / S)$.

In this paper the methods of calculation of true adhesive strength will be considered. The approach is based on the data of traditional simple experiments and on the theories that consider the stress-strain state at the interface. In such consideration the theory of boundary layer and the shear-lag analysis in both analytical and numerical (finite elements) versions are used.

The questions of estimation of durability for the same types of adhesive joints will be also discussed.

EFFECT OF INTERLAYER BETWEEN AMORPHOUS AND CRYSTALLINE PHASES ON THE MECHANICAL AND THERMOELASTIC BEHAVIOUR OF POLY(ARYL ETHER KETONES)

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In recent years much research has been devoted to exploring the potential advantages of thermoplastic matrices for composite materials. One such matrix class – poly(aryl ether ketone) (PAEK) – shows exceptional properties due to its semicrystalline character and the molecular rigidity of its repeating units. PAEK materials, isothermally crystallized from the melt or annealed from the glass, reveal double-melting endothermic behavior. Two melting peaks are observed, one about 20 °C above the crystallization temperature, and a larger one at higher (melting) temperature. This behavior has variously been explained as resulting from 1) kinetics of melting/recrystallization processes during a DSC scan and 2) the influence of secondary crystalline structure. In particular, the existence of the morphology-dependent rigid amorphous fraction (RAF) in the amorphous phase of semicrystalline polymers was discussed by Wunderlich¹. RAF properties differ from those of crystalline and amorphous fractions of semicrystalline polymer. It behaves like interlayer between amorphous and crystalline phases and its contribution to the mechanical properties of a semicrystalline polymer may be important.

The objective of the present study was to relate the bulk mechanical behavior of PAEKs to their micro structure and in particular, to the existence of RAF. PAEK samples of various micro structure were available as a result of (i) different thermal treatment and (ii) choice of PAEKs with different ketone content.

The double-melting behavior PAEKs was detected by differential scanning calorimetry DSC experiments. The samples tested were poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK), which were annealed from the glassy state at different crystallization temperatures T_c . The size and location of premelting peaks on DSC tracks were affected by T_c , provided that $T_c > T_g$. An influence of T_c on the mechanical behavior of stretched PEEK and PEK (uniaxial deformation mode at 200 °C) was also observed. The perfection of crystalline structure was thought to be a reason for this influence.

Thermoelastic experiments at room temperature, comprising simultaneous measurements of the mechanical work and of the concomitant heat, were performed on semicrystalline PAEKs. This study uses the sensitive thermoelastic technique to examine PAEK thermoelastic properties as a function of the relative abundance of ketone groups on different PAEKs. The effect of PAEK micro structure on thermoelasticity at room temperature was insignificant. This was attributed to the dominant contribution of immobile amorphous phase on thermoelastic properties.

It is expected² that thermoelastic measurements, carried out at $T > T_g$, may clarify RAF influence on the mechanical behavior of PAEKs.

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* The author thanks the Alexander von Humboldt foundation for the support of this research.

Effects of Silane Coupling Agents on Interphase and Properties in Glass-Fiber Reinforced Composites

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ABSTRACT

The properties of the fiber-matrix interphase in glass-fiber reinforced composites can play a dominant role in governing the overall composite performance. Understanding the interactions occurring at the interphase and being able to tailor them to give a desired composite property is of great importance. In this paper, a single-filament mimic of a commercial fiberglass reinforcement manufacturing process was used to apply methacryloxy silanes with one, two and three silanols (mono-ol, di-ol, and tri-ol) to calcium-alumino-silicate glass fibers. Surface analyses by ADXPS and contact angle measurements with two liquids were used to characterize the coatings. Single-fiber fragmentation tests were used to evaluate interfacial adhesion. Changes observed in surface chemistry, single-fiber fragmentation tests, and composite mechanical properties as a function of the type silanol will be discussed.

SURFACE RECONSTRUCTION OF PHOTOOXIDIZED EPDM RUBBER: KINETICS AND MECHANISM

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Surface reconstruction (rearrangement) plays significant role in polymer biocompatibility and adhesion. Such reconstruction may occur when the chemical composition of polymer surface layer is changed in comparison with the bulk one as a result of modification by grafting, plasma treatment, etc. The same effect can take place upon variation of the polarity of the medium contacting with polymer. In both cases, the main driving force for such reconstruction is minimization of the surface (interfacial) free energy. The kinetics of this process depends on its mechanism, which may be different for distinct systems and determined by macromolecular (segmental) diffusion and/or reorientation of individual groups.

We have studied the surface reconstruction of thin casting films of the EPDM rubber after their photooxidation in air and, by using IR spectroscopy and wettability methods, obtained the following main results.

1. At early stages of photooxidation, when the concentration of polar oxygen-containing groups formed is relatively low, these groups are quickly buried into the bulk from the polymer surface and surface energy does not increase. On the contrary, certain decrease of the surface energy takes place, apparently due to "loosening" of the polymer surface layer during its rearrangement.

2. When air is replaced by water or another polar liquid, the "reverse" reconstruction of the surface layer of photooxidized rubber occurs. It means, that oxygen-containing groups gradually emerge at the polymer/liquid interface. The rate of this process and the degree of the interfacial free energy lowering depend on irradiation dose (i.e. on content of polar groups in the rubber film).

3. As followed from the analysis of the experimental data obtained by "prolonged wetting" method, such reverse reconstruction accompanying by the polar groups accumulation at the photooxidized rubber/water interface can not be described within the framework of the simple model of polar group reorientation (turnover) but it is a diffusion-controlled process.

This conclusion is consistent with the results obtained for the prevulcanized EPDM films. For such films, even at low degrees of photooxidation, no surface rearrangement was detected; the polar groups formed were remained at the polymer/air interface, obviously owing to the loss of macromolecule translational mobility in surface layer.

SELF-REARRANGEMENT OF THE TRANSITION COMPOSITION ZONE OF POLYMER-METAL JOINTS IN WATER

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The increase of strength of adhesive joints or coating systems after their exposure to hot or boiling water have been observed by different groups of researchers. However, up to the present the causes of this effect are not completely clear. Our earlier data on the long term stability of epoxy polymer-aluminium coating systems showed that the storage of these systems in water at various temperatures at first leads to an essential decrease in the peel strength followed by the recovery of strength without drying the systems. In order to apply this effect in practice, the stage of strength decrease should be diminished or precluded. To do this it was necessary to study the mechanism of the effect, as well as to determine kinetic parameters of the processes involved. Using a peel test, sorption of water, transmission and reflection-absorption FTIR spectroscopy, transmission electron microscopy and electron diffraction techniques we determined the rates of water diffusion into the interface of coating system, rates of hydrolysis of interface bonds and hydration of aluminium oxide. A new method was proposed to evaluate the rates of hydrolysis and hydration. It is based on determination of the critical peel rate of coating system containing drops of water inserted into the capillary formed by coating and metal at which the influence of inserted water on the peel rate is stopped. Comparison of diffusion rates for the samples with different thicknesses of coating and various metal surface pretreatments, with the rates of hydration process led to the conclusion that the first process is of major significance in failure of joint. It was also investigated the changes of chemistry and morphology of transition composition zone which occur during exposure the systems to water. It was found that aluminium migrates into the epoxy polymer during preparation of coating system. Therefore, after immersion of the system into water hydration process is started both in the bulk of coating (in the vicinity of the interface), and on the surface of metal contacted with polymer. During next several hours of storage a new transition composition zone is formed. It consists of the initial interface covered with aluminium hydroxide and a layer of ordered microcrystals of hydroxide separated from the interface by the 3 micrometers thickness layer of polymer filled with microcrystals of aluminium hydroxide (boehmite).

THE ROLE OF INTERFACIAL DEBONDING IN FATIGUE OF POLYMER COMPOSITES

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Fatigue in the longitudinal direction of CF/EP composites did not take place when only low strain to failure carbon fibers and brittle matrices were used. As carbon fibers with higher strain to failure and more ductile matrices have been introduced, longitudinal fatigue does take place. Furthermore, the longitudinal plies have been shown to control multidirectional laminate fatigue. Results in the literature show that tougher resins in general show poorer fatigue properties in the longitudinal direction. Since the fibers themselves show no fatigue mechanism, the explanation must be sought in failure mechanisms taking place in the matrix or at the fiber/matrix interface.

The present study is focused on the mechanisms for arrest of damage in the material. It is demonstrated that interfacial debonding plays a key role in this context. Damage mechanisms have been documented by surface replicas taken after a certain number of cycles. Mechanisms of damage progression around fiber breaks have been observed and are discussed.

IDENTIFICATION OF THE YOUNG'S MODULUS OF THE INTERPHASE IN GLASS/EPOXY COMPOSITES

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The interphase in fibre reinforced composites depends on the fibre, the matrix and the surface treatment of the fibre. Many investigations were done with industrial fibers with an unknown content of sizes or resin. Thanks to the cooperation between the Ciba Geigy GmbH and the Institut für Polymerforschung e.V. Dresden, Germany we were delivered with fibres, sizes and resins of known ingredients.

A gradient in the epoxy to curing agent ratio is created in the interphase by the surface treatment (coupling agents or epoxy finish) or possible chemical reactions (the hydroxyl group or water reacts with the curing agent) . Depending on this, the mechanical properties in this region are changed. We will describe the changes of the properties especially for the Young's modulus and the Poisson's ratio in the interphase with a self-developed mathematical model.

For composites under tension transverse to the fibre direction the Young's modulus has been determined for composites with different treated glass-fibres, differently cured epoxy resins and with a different content of fibre volume. Static tests on this composites were made and a model for the Young's modulus of the composite which includes the interphase was developed. The computer program was developed in cooperation with the Institut of Computer Analysis of Structure, TU Riga*.

The results of the tests and the model were compared and an average Young's modulus of the interphase was identified.

SHORT ARAMID-FIBER REINFORCED ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE

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Ultra-High Molecular Weight Polyethylene (UHMWPE) is frequently used in artificial joints because of its high wear resistance. The current clinical practice of using UHMWPE as hip-joint prostheses in younger patients, with an expected lifetime more than 20 years, has generated renewed concern about the wear and durability of UHMWPE. To extend the lifetime of these joints even further, it is necessary to decrease the wear rate. The wear rate may be decreased by blending UHMWPE with short aramid fibers. On account of the extremely high viscosity of UHMWPE mixing was accomplished by swirling the UHMWPE powder and the chopped fibers with compressed dry nitrogen, and a composite with fairly uniformly distributed and randomly oriented fibers was obtained by compression moulding. The failure behaviour of the composite changes from ductile for low fiber content to brittle failure for higher fiber content.

Voids in materials are an important cause of loss of strength and premature failure. Voids in short-fiber polymer composites may arise from entrapped air introduced during the compounding and processing stages inside fiber agglomerates, which are difficult to break up and to eliminate during compression moulding. In general, the void content increases with fiber concentration. Voids are observed even in unfilled UHMWPE, indicating that the fiber's presence is not necessarily the only source of voids.

The deviation of the experimental Young's modulus from the theoretical value can be explained by, among others, the void content. The theoretical Young's moduli are calculated with the well-known 'rule of mixtures' equation: $E_c = \eta_0 E_f V_f + E_m V_m$ with E the modulus, V the volume fraction, the subscript f and m refer to fibers and matrix respectively, and η_0 the orientation factor. $\eta_0 = 3/8$ for in-plane random fiber distributions and $\eta_0 = 1/5$ for a three-dimensional random distributions. Taking the void content into account, the volume of the composite can be defined as: $V_c = V_f + V_m + V_v$. Because of this volume change, the volume fractions in the rule of mixtures change to lower values, which cause lower theoretical moduli. The remaining deviation is caused by the difference in Poisson contractions of the fibers and the matrix, fiber length and fiber ends, and packing defects.

A pin-on-disk method has been applied to determine the wear rate of UHMWPE and UHMWPE/aramid composite.

MODEL POLYCONDENSATES FOR THE MATRIX-GLASS FIBER INTERPHASE

I) HUMID AGEING OF SYSTEMS CONTAINING AMINE, EPOXIDE OR ALKYL GROUPS.

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Polycondensates of trialkoxysilanes of the type (Alk-O-)SiR in which the R group is respectively ended with an amine (APS), an epoxide (GPS) or an alkyl group (PS) have been prepared by hydrolytic crosslinking in order to obtain solids simulating an important interfacial layer in amine crosslinked epoxy-glass fiber composites.

Analytical studies have revealed a high conversion degree of crosslinking in the three samples. They have been submitted to wet ageing in various conditions (temperature from 0 to 100°C, relative hygrometry from 0 to 100%), and their composition and structure changes have been monitored by gravimetry. Hydrophilicity has been found to be sharply related to the polarity of R group:

APS>GPS>>PS.

Under relatively soft conditions, the critical physical sorption step can be decoupled from further hydrolysis, which allows to estimate the water solubility and diffusivity in these materials.

It can be concluded from these values that they cannot act as barriers protecting the fibre surface from water.

APS and GPS materials are reactive toward water. Their hydrolysis is relatively fast in the conditions under study. It is however an equilibrated reaction.

A first kinetic model is proposed and the consequences on composite wet ageing are discussed.

Key Words: Composites, Interfaces, Epoxy, Glass fibre, Interface, Model compounds, Coupling agents, organosilanes, Humid ageing.

INFLUENCE OF GRAFTS LENGTHS ON ADHERENCE AND MOISTURE AGEING IN CELLULOSIC FIBRE / POLYPROPYLENE MICROCOMPOSITE

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The aim of this study is the optimisation of the adhesion in a composite made of cellulosic fibres and a polypropylene matrix. The fibres are chemically grafted with alkyl chains of various lengths (aliphatic isocyanates : R-NCO) or modified polypropylene chain (polypropylene grafted with maleic anhydride : PPgMA).

All the grafted fibres were soxhlet extracted before being in contact with polypropylene in order to take into account the effectively grafted chains only.

In swelling medium, the R-NCO grafts penetrated into the cellulosic fibres. The mechanism of water sorption (water uptake and kinetics) is then modified. A combination of fast and slow diffusion paths allow the explanation of the water accessibility of the cellulosic fibres microstructure : the location of grafts useful to the decreasing of the fibres hydrophilicity is then possible.

The adherence, measured by the micro-bond test, is especially discussed here as a function of the nature of grafting. Two different failure behaviours can be noticed : the failure is initiated by a constant shear stress in the case of R-NCO treated fibres. In the case of PPgMA treated fibres, a constant force is noticed whatever the size of the embedded area.

The microcomposite durability is controlled after moisture ageing : a maleated polypropylene (PPgMA) improve the adherence but does not resist to moisture ageing. Alkyl chains (8 to 18 carbons) decrease the water sorption and give to the fibres an hydrophobic behaviour. Meanwhile, no improvement of the adherence is observed but the standard deviation of the measurements is decreased : the interface is better controlled.

At end, which species to graft ? The best systems could be **double-grafted** ones :

- 1 - creation of a high modulus interphase with PPgMA grafting agent,
- 2 - improvement against moisture ageing by a treatment with a small molecule aiming to give to the fibre a better dimensional stability.

CHARACTERIZATION OF THE FIBRE-MATRIX INTERFACE WITH THE INDENTATION TECHNIQUE

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When characterizing a composite, three levels of abstraction related to the scale levels can be distinguished: With the most general point of view, a composite appears as a continuous, homogeneous, but anisotropic material. On the "microscopical" level, the characteristics of the reinforcement have to be taken into account, such as the geometry, orientation and distribution of the fibres in the matrix. Finally, on the "nanoscale", the structure and morphology of the fibre and matrix bulk material as well as the interface and 'interphase' between them are parts of the entire composite. Since the relations between these different scale levels can be very complex, it is recommendable to investigate phenomena of each scale level separately before discussing the influence of one factor on the entire material.

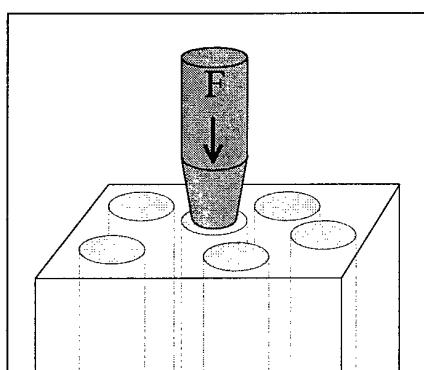


Fig. 1: Schematic diagram of the indentation test

The indentation test^{1,2} is designed to characterize one important factor of composites on the "nanoscale" level: the interface between fibre and matrix. For polymer matrix composites it is not as widely used as the fragmentation test, the single fibre pull-out test or the droplet strip-off test, although it has some interesting features, which may overcome intrinsic problems of these methods:

- All fibre-matrix combinations can be tested except with fibres, which are sensitive to compression (e.g. poly(ethylene), aramide and some natural fibres).
- The indentation technique allows to test interfaces 'in situ' in multi-fibre composites. For example, it can be investigated, whether processing conditions were

suitable for chemical bonding reactions, whether long-time loading under realistic conditions or an aggressive environment affects interface properties inside a practically used composite.

- An energy balance instead of a strength criterion is used for analysing the test data. This avoids a common problem of all micromechanical tests: the estimation of the unknown maximal stress arising in the interface. With the energy balance criterion, the surface energies of covalent and adhesion bonding as well as the friction stress of an already debonded interface can be determined separately.

Because the theory of Marshall and Oliver¹ does not respect compliant matrix composites, model calculations were performed to analyse the interfaces of reinforced polymers. To ensure accurate measurements, an advanced test apparatus with a sufficiently high stiffness was developed.

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EFFECT OF SIZING AGENT ON INTERFACIAL PROPERTIES OF ARAMID KNITTED STRUCTURAL COMPOSITES

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ABSTRACT

This study presents an evaluation of the effect of sizing agents on tensile property of aramid knitted structural composites. An objective of this study is to clarify the micro and macro fracture mechanism of the sized aramid knitted structural composites subjected to a tensile load. The performance of knitted structural composites is closely related to failure of fibre bundle during knitting process, strength of knitted fabrics and the interfacial properties between the reinforcement and the matrix. Although considerable studies to improve the fibre-matrix interface have been reported so far, there are very few studies on the effects of surface treatments of knitted structural composites by considering these factors.

The span aramid yarns(KEVLAR 49) were weft knitted on a flat knitting machine to produce plain knitted fabric. Two kinds of sizing treatments were performed; one was a polyethylene type sizing agent on the weft knitted fabrics and the other was an epoxy type sizing agent on the knitted fabrics refined by cyclohexane. Matrix used was a bisphenol-A type epoxy resin. Flat plate with one knitted fabric was fabricated by hand-lay up method. Tensile specimens were cut out according to both course direction and wale direction. The tensile tests were performed at 0.05 mm/min cross head speed and the fracture of specimen was monitored by a video camera.

The tensile strength of epoxy sized knitted structural composite was higher than that of polyethylene sized composites in both wale direction and course direction. In our previous works, the tensile strength in wale direction is higher than that in course direction in weft knitted fabric reinforced composites. Moreover, two fracture modes were in the tensile property; that is fracture occurs at the section with extreme low fibre content corresponding to the arc part of knitted loop in course direction and fracture occurs due to stress concentration at loop interlocking region in wale direction. The effects of these sizing systems on the tensile property and the fracture mechanism of the aramid weft knitted structural composites are discussed.

CHARACTERISATION OF THE LEWIS ACID BASE BEHAVIOUR OF MODIFIED
POLYOLEFINE SURFACES BY MEANS OF FLOW SORPTION
MICROCALORIMETRY AND INVERSE GAS CHROMATOGRAPHY

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In many fields of polymer science, i.e. composites and blend formulation, interfacial interactions play an important role. The strength of the macroscopic adhesion is proportional to the microscopic interfacial energy change. The magnitude of interfacial forces may range from strong covalent bonds to rather weak van der Waals interactions. But in many systems of interest, chemical bonds are absent and that's why the thermodynamic work of adhesion between two phases is due to physical forces. According to Fowkes, such interface interactions may be assigned to dispersion and electron donor-acceptor interactions. Most polymers, except for saturated hydrocarbons such as polyethylene or polypropylene, have functional sites which may act as electron donors or acceptors. But especially these polyolefines are important in the field of composites and blend formulation because of the enormous amount produced world wide. One way to realize a good interfacial adhesion between these non polar polymers and polar fillers, reinforcing fibers or pigments etc. is to enter polar, i.e. acidic or basic modified PE or PP.

The aim of the work was to test the usefulness of flow sorption microcalorimetry, in order to determine the acid base strength of differently modified PE and PP powders. Their heat of interaction with basic or acidic probe molecules from dilute solution in a neutral solvent, was calorimetrically measured simultaneously with the amount adsorbed onto the polymer (frontal analysis).

In addition to this method, these polymers were investigated by means of inverse gas chromatography at infinite dilution, in order to determine the heat of adsorption of acid and base probe molecules. A comparison of the results obtained by calorimetry, inverse gas chromatography and x-ray photo electron spectroscopy will be shown.

Session 2A

The Polymer Interphase in Composites: Intrinsic Limitations to Adhesion

by

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Abstract

Adhesion between fiber and polymer matrix is the result of a complicated set of interactions which takes place near the fiber surface. The exact nature of this interaction is thought to be the result of chemical, physical and topographical factors. In order to determine the nature of these chemical, physical and topographical interactions, a series of PAN-based carbon fibers treated to various surface treatment levels were prereacted with chemical compounds representing the constituents encountered in a typical epoxy matrix during conventional processing cycles. Only monolayer quantities were used to allow direct observation of the changes in fiber surface chemistry. In this way reactions could take place which could be quantified by X-ray surface analysis. The prereaction with compounds containing epoxy functionalities were found to enhance adhesion while those with amine functionalities were shown to have a very minor effect. Prereaction with monofunctional groups effectively blocked all available surface sites and allowed the role of chemical bonding to be independently assessed. Quantitative measurement of the fiber surface topography was conducted on these same fibers with scanning tunneling microscopy. A direct relationship between the quantity of chemical groups on the fiber surface and the increase in microtopographical area was found indicating that both chemical and mechanical factors contribute to fiber-matrix adhesion in composites. Temperature dependent measurements of interfacial shear strength were useful in determining the balance between interfacial and matrix properties that contribute to the measured values of interfacial shear strength.

SPECIFIC COUPLING AGENTS FOR PROMOTING ADHESION BETWEEN CONDUCTIVE POLYPYRROLE AND GLASS FIBERS SURFACE.

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Coating reinforcement material with a layer of an electronic conductive polymer, for instance polypyrrole, offers a new and original way of elaborating conductive composite materials. But this principle comes up against the poor adhesion generally noticed between bare glass surfaces and conductive polymer deposits, inducing poor mechanical performances for the material.

Such a difficulty has been overcome by using specific silane coupling agents, specially synthesized for promoting adhesion between glass and polypyrrole (1). These novel compounds are easily prepared from commercial aminosilanes and pyrrole derivatives; by this way, they give the possibility to bind, to the surface of glass, pyrrole groups, which are anticipated to be later included into a growing polypyrrole chain, when pyrrole is subjected to polymerization in the presence of such silanized fibers.

Solubility, hydrolysis, and self-condensation features of these silanes, which have been investigated by FT-IR, ^1H and ^{29}Si NMR spectroscopies, make them easily compatible with current industrial procedures.

Varying the experimental conditions of pyrrole polymerization on pretreated glass surfaces allows conductivity control. An unexpected effect of the presence of pyrrole-substituted silane is an enhancement of the conductivity, when compared to using commercial coupling agents (amino-, acryloyl-, or glycidyl-substituted silanes for instance). In order to explain this effect, morphological SEM and TEM examinations, XPS analysis and Raman spectroscopy have been used.

Pull-out tests on coated monofilaments, and interlaminar shear strength measurements on organic matrix laminates, demonstrate likewise that the presence of an intermediate conductive layer, when anchored to the glass fibers by the specific silanes, does not induce in any way a loss of fiber-matrix adhesion, contrarily to what happens when regular coupling agents are used.

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PLASMA TREATMENT AND ADHESION PROPERTIES OF IMPACT-MODIFIED POLYPROPYLENE

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Cold, glow-discharge plasmas were used as a pretreatment method for lacquering impact-modified polypropylene (TPO) surfaces. Studied were the effects of microwave (MF), radio RF) and of combined MF and RF frequencies, along with the effects of power to flow ratios (P/F). Discharge gases included oxygen, nitrogen air, argon and hydrogen. Surface characterization was by contact angle and XPS analyses. Adhesion between plasma-treated TPO surfaces and a two-component polyurethane lacquer was measured by 180° peel tests. The wettability of TPO was unaffected by variations in plasma frequency or P/F, but choice of discharge gas was shown to be important. No correlation could be defined between wettability and adhesion. Instead, lacquer adhesion was highly dependent on P/F and on the choice of plasma gas. The locus of cohesive failure in all assemblies was invariably in the substrate. Electromagnetic radiation, most likely vacuum-uv emission, was proposed to be a critical factor in plasma treatment. Uv-radiation was suggested as the source of free radical in the TPO substrate; chain scission reactions would ensue, thereby governing the cohesive strength of the near-surface interphase of the substrate.

A PSEUDO-ENERGY BASED METHOD TO PREDICT FIBRE-MATRIX ADHESION USING A SINGLE FILAMENT COMPOSITE

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The fragmentation test is now commonly used for measuring the fibre-matrix adhesion in a single filament polymer composite. It is now widely accepted that the data reduction techniques for the fragmentation test based on the constant shear model of Kelly-Tyson and the partial debonding model of Piggott are inaccurate, hence, reinterpretation of the results is required. Recently, we have introduced a pseudo-energy based technique to calculate Cumulative Stress Transfer Function (CSTF) value from the fragmentation test data which is used as a measure of the interface quality. This technique offers several advantages over the existing data reduction techniques and is based on an accurate stress transfer model, the plasticity effect model of Tripathi and Jones, for predicting the stress profile in a single discontinuous fibre composite. This model can also be used for predicting the interfacial adhesion where debonding occurs at the fibre-matrix interface. In this method, the interfacial shear stress associated with and the tensile stress in the individual fragments are predicted from the plasticity effect model and the total tensile stress transferred to all of the fibre fragments at a particular matrix strain is calculated. The total tensile stress transferred to all of the fibre fragments normalised against the fibre length is defined as the cumulative stress transfer function. The technique is further refined to take three dimensional yielding of the matrix and modified stress transfer in the debonded region into account. The purpose of this paper is to present the details of these refinements and, closely analyse and interpret the results from more fragmentation tests. The fragmentation of single glass fibre with different coupling agents in epoxy resin at different applied strains have been used to validate the applicability of the CSTF technique at an applied strain which is less than the strain required for the saturation in the fragmentation process, thereby, overcoming one of the major limitations of the fragmentation test.

OBSERVATION OF TWO GLASS TRANSITIONS IN FILLED POLYMERS

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On the basis of the mechanical properties of random ionomers, it had been predicted recently that filled polymers should exhibit two glass transitions, provided that the size of the filler particles is very small and that strong polymer-filler interactions are present. Indeed, it was found that several polymers including polyvinylacetate, polystyrene, polyvinylpyridine and polydimethylsiloxane, when filled with more than 10wt% fine silica particles, have two glass transitions. This finding has important implications to composite systems, where the polymer-solid interface determines to a large extent the overall properties. For various composite systems, e.g. filled polymers, solid or liquid polymer films on solid surfaces, it has been shown that polymer chains residing at the polymer-solid interface experience mobility restrictions. The properties of ionomers, which in most cases exhibit two glass transitions, have been explained by the EHM model to originate from the overlap of regions of restricted mobility (clusters) which are formed around the ionic aggregates (multiplets). Subsequently, it was found that if clusters were regarded as a filler phase, the ionomer modulus followed the Guth equation. It was with these findings in mind, that the dynamic mechanical properties of various polymers filled with fine silica particles were measured. The results showed that filled polymers, containing more than 10wt% silica, in analogy to ionomers, exhibit two glass transitions, one being the usual polymer glass transition, and the other, at a higher temperature, originating from overlapping regions of restricted mobility. This assignment was based on the activation energy of the second transition, and the way it is affected by the polymer molecular weight and the strength of the filler-polymer interaction. As the particle content increases, the second Tg and the area of the $\tan \delta$ curves decreases, indicating that the mobility restrictions are relaxed; however, a smaller amount of polymer participates in the two glass transitions. When the average molecular weight of the polymer decreases, the second Tg decreases, since the shorter chains are less able to bridge two filler particles and form fewer contacts with the filler surface than longer chains. When the filler content is below 20wt%, the thermal history of the sample affects significantly the second Tg and the area of the corresponding $\tan \delta$ peak. A new model is proposed, which takes into account the formation of tightly bound (immobile) and loosely bound polymer chains around the filler particles, and is also based on the concept of overlapping regions of restricted mobility, as described in the EHM ionomer model. When the filler content is less than 10wt%, the regions of restricted mobility do not overlap, and hence no new glass transition is observed. At 10wt% silica content, the loosely bound polymer chains around different particles begin to overlap and a second glass transition appears. As the filler content increases, more restrictions are imposed on the mobility of the loosely bound chains and these become progressively immobilized. Thus, an increasing amount of the polymer cannot participate in the two glass transitions, and the area of the two $\tan \delta$ peaks decreases. Since the loosely bound polymer chains experiencing the greater mobility restrictions will be the first to be transformed to tightly bound material, the second Tg decreases as the filler content increases.

Session 2B

Study of microstructure and interfacial properties of composite materials prepared with alkali resistant silicate glass fibres and alinite cement and other hardened cementitious matrix materials

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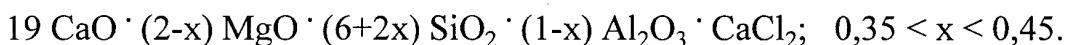
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Abstract

Filaments of AR glass were tested in respect of their application in glass fibre reinforced composites with a matrix especially of alinite cement. Matrix properties and the result of the fibre matrix interaction were compared with these composites containing a matrix of ordinary Portland cement (OPC) or a matrix of chemically modified Portland cement using microsilica (DURAPACT®). Under identical experimental conditions such as treating time, temperature and humidity, the silicate glass fibres and fibre matrix interfaces were examined by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA).

The formation reaction of Portland cement clinker (mineral alite = $3\text{CaO} \cdot \text{SiO}_2$, C_3S) is realized at temperatures > 1200 °C. In opposite to this a low temperature processing (< 1200 °C) of a cementitious material is realized by the synthesis of alinite as the dominant mineral phase with its theoretical chemical composition



Such a matrix is not suitable for composites with a reinforcement manufactured with steel and steel fibres. But the content of chlorine ions has no negative influence if there is a reinforcement with silicate glass fibres as those of the $\text{Na}_2\text{O-ZrO}_2-\text{SiO}_2$ system.

THE ROLE OF THE INTERFACE IN BRAZED METAL/CERAMIC LAMINATE

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ABSTRACT

The mechanical behavior of composites is governed by the interfacial strength or toughness after a damage in the brittle constituent is initiated. 'Strong' interface resulted with low longitudinal strength (local load sharing) but good transverse strength, while 'weak' interface is characterized by stronger longitudinal strength (global load sharing) and low transverse strength. The interface, therefore should exhibit intermediate properties.

The discussed composite is a relative new type of composite, constructed from multilayered metal/ceramic brazed laminate. Layers of Ti-6Al-4V alloy and alumina, both with thickness of about 1 mm, were joined using AgCuTi active brazed alloy (Wesgo Cusil ABA), in low pressure, low temperature, low vacuum process. The volume fraction of the ceramic layers within the laminate is ranged between 25 to 35%. The thickness of the brazed alloy is 50 μm .

Such system is expected to be characterized mainly by in plane isotropic undamaged strength and modulus, high specific strength and modulus, high toughness, improve strength of each constituent, and above all - at relatively low cost. The laminate is expected to serve in intermediate temperature, without significant reduction in mechanical properties.

The interface plays an important role in the mechanical behavior of the laminate. Strong interface will increase the strength for first failure of the ceramic layers and enhanced the yield point of the metal. Furthermore, it governs the mechanical behavior after damage in form of cracks occur in the ceramic layers.

The toughness of the interface will be reported. The interface properties were analyzed using four point bending of bimaterial beam and by means of tensile specimen. The failure mechanisms will be discussed.

The response of the metal/ceramic laminate in bending and tension will be present. The enhancement of mechanical properties due to mutual constrained layers and the role of the interface in the overall behavior will be discuss.

EVALUATION OF THE INTERFACIAL BONDING PROPERTIES IN DIFFERENT GRADATION FOR C/C COMPOSITES

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The interfacial bonding property of carbon fiber reinforced carbon matrix composite and its correlation to the material processing technology and to the macroscopic mechanical performance have been gradually concerned by C/C composite research workers. For multi-directional C/C composites, a concept of different graded interfaces was proposed initially by the authors, which consists of $I_{(1)}$ meant the interface between an individual whole fiber bundles and its surrounding carbon matrix, and $I_{(2)}$ meant the interface between an individual fibers and its surrounding carbon matrix in every fiber bundle. This paper introduced some results of preliminary quantitative research in the above two kinds of interfacial bonding properties for narrow-braided-pierced C/C composite materials, by using the recently developed techniques of push-in (microdebonding) and push-out tests.

Narrow-braided-pierced C/C composite materials with different impregnating pitch processing parameters of 3-D performs were used to investigate the evaluation of different graded interfacial bonding properties, and to find their effects on the macroscopic mechanical properties of the composites under different processing parameters. Specimen for interfacial test was prepared by cutting a small piece (typically 1.0 mm thickness for $I_{(1)}$, a bundle push-out test or 3.0 mm thickness for $I_{(2)}$, microdebonding test) from C/C composites, perpendicularly to Z-directional fiber bundles. Polishing the cutting surfaces using conventional metallographic techniques. In the test, a compressive load was applied axially to the end of a bundle or single fiber until interfacial debonding occurs. The load at debond, recorded by computer, was input to a finite-element program, which calculates the interfacial shear strength.

The general results show that the bonding strength of $I_{(2)}$ has the same tendency with the Z-directional macroscopic tensile strength of C/C composite, while the bonding strength of $I_{(1)}$ just has an opposite tendency. Further studies indicate that a mate problem between $I_{(1)}$ and $I_{(2)}$ do exist. This reveals that the different graded interfacial bonding status may provide completely different contributions to the mechanical properties. This is very important for the material design.

Using the push-in and push-out techniques to measure the interfacial properties of C/C finished and semi-finished products on the purpose of quantitatively studying the relations of the C/C composite processing technology, the interfacial properties and the macroscopic properties, we may find the crucial working procedure affecting composite interfacial properties and else obtain the optimal interfacial bonding property value of high property C/C composite product in order to stabilize and improve product quality.

Ca SEGREGATION TO BASAL α -ALUMINA SURFACES AND ITS ROLE AT METAL-CERAMIC INTERFACES

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Microstructural design objectives for metal-ceramic joints and composites are often limited by the nature of the metal-ceramic interface. Two very different materials must be joined with a specific interfacial geometry, and a physico-chemical bond must be formed between them. In brazing and composite processing the quality of this bond is often limited by the process of wetting of the ceramic by a *liquid* metal, and this process may include the formation of interface phases due to chemical *reactions*, both between the components and with the process atmosphere. These issues have been addressed in a study of α -Al₂O₃-Al interfaces formed within melt-infiltrated composites. The composites were prepared by the infiltration of liquid Al at 1050°C into a sintered α -Al₂O₃ preform. Conventional TEM revealed no wetting-defects (residual interface porosity), even though Al does *not* wet α -Al₂O₃ (contact angle greater than 90°). In order to understand this effect, high resolution transmission electron microscopy (HRTEM) and analytical electron microscopy (AEM) were applied to characterize selected interfaces in these composites.

HRTEM of (0001) α -Al₂O₃-Al interfaces consistently revealed an interfacial region with a *structural width* of 0.8±0.2nm. AEM of the *same* interfaces revealed a Ca excess of $\Gamma=2.5\pm0.5$ Ca/nm². AEM of a basal twin boundary in the α -Al₂O₃ also revealed a Ca excess ($\Gamma=1.0\pm0.5$ Ca/nm²). Since the metal-ceramic interfaces were the free surfaces of pores before melt-infiltration, it can be concluded that Ca segregates to the basal surface of Al₂O₃, as well as to basal twin boundaries. This contradicts previous studies which claimed no Ca segregation to basal surfaces. Furthermore, the Ca at the free surfaces does not reside on only one cation plane, but is spread over 4±1 basal cation layers, and thus forms a 0.8nm thick interfacial phase with a *nominal* composition of CaO·6Al₂O₃. The presence of the surface phase would be expected to alter the *contact angle* of Al on Al₂O₃, and may explain the lack of wetting-defects in the composite.

Session 3A

Silane Coupling Functions and Fracture of Composites

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In order to clarify the effect of silane coupling agents on mechanical properties of glass fiber composites, it is necessary to have a couple of approach from molecular structure near the silane-treated glass fiber and from mechanical properties of composite interfaces. First, we have studied the fixation of silanes to glass fiber using pyrolysis GC/FT-IR [1-2]. This technique has shown the minimum amount for forming the network of silane deposit linked to the surface of glass fiber. This result depends on industrial procedure in silane treatment for glass fiber, 'dip-cure'. Second, we have been studying the interfacial effect on single filament embedded in matrix resin. As a result, the initial microfracture along filament has been found to understand the relation between interfacial structure and mechanical functionality at the interface. As proposed using the first microfracture in our papers[3-5], an interfacial parameter, 'interfacial transmissibility' is useful to clarify the interfacial effect. The initial microfracture reflects the structural property at silane-treated interface. Such a change is related to the silane fixation. A small quantity of fixed silane little produces interfacial reinforcement, while much higher fixation gives the silane networks that prevent the penetration of resin into the silane interphase. This result suggests that silane network structure is a dominant factor in penetration of resin molecules into silane networks. Third, we have developed the technique to measure the initial microfracture in single ply of fabric composite [6]. This technique gives a parameter, 'initial microfracture stress'. The change of initial microfracture is similar to that of interfacial transmissibility. This means that the interfacial effect appears under the same mechanism regardless of fabric structure, even though the magnitude of interfacial effect is significantly changed by the tensile direction from warp to weft. From these results, interfacial effect should be correlated to the initial microfracture, neither to fracture process nor fracture strength. Recently, we have studied the mode II fracture of rod-type uni-directional glass fiber composites. The fracture toughness keep constant, even if only the fixation of silane on glass fiber is changed at the same amount of the silane deposit. Such a dynamic property seems to be related the property of matrix resin near silane-treated glass fiber. We have already detected the changed area of resin affected by silane deposit on glass fiber using microscopic FT-IR [7]. This denatured area is widely produced in micron-order, and depends on only the amount of silane on glass fiber, regardless of the fixation. These results suggest that the initial microfracture exhibits the interfacial strength due to silane coupling function through chemical bonds and that the fracture process reflects the local environment of silane to resin matrix.

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FIBER SURGACE MODIFICATION IN GLASS-EPOXY PULTRUSION

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Flexural and dynamic-mechanical properties of glass-epoxy pultruded composites are studied as the glass fiber surface is changed.

Commercial E-glass fiber are, first, washed in methyl-ethyl-ketone (MEK) in order to eliminate non-reacted sizing agents, and then, they are treated with two modifiers: o-cresyl glicidyl ether (CGE) and 1-4 butanediol diglycidyl ehter (DGEBD). Both are diluted at several percentages in MEK to improve fiber impregnation and fiber surface modification. A different interfacial thickness can be obtained with each solution. Finally, the solvent is evaporated.

Composites are obtained pulling the fibers through a resin bath (epoxy matrix) and placing them into a rectangular section mold, where the complete system cures and adquire dimensional stability. Fiber volumen fraction is kept constant.

Samples are cut to meet three point bending test requirements (ASTM standars). The relation span-sample thickness (L/d) is varied to determine how the shear stresses change.

Results allow to confirm that there is a (L/d) value at which the interfacial influence becomes more important due to the differences in the shear stressesmeasured for samples with different surface treatments. Test must be run with (L/d) values less than 10 in order to perceive changes from glass surface modification.

The bending stress presents a maximum as the coating thickness increases for the CGE treated fibers. However, in the case of DGEBD treatment, the flexural stress decreses as thickness increases.

Dynamic-mechanical analysis (DMA) is perform using a three point bending fixture. Preliminar results do no show a transition peak due to the presence of the interphase in the composite. Using fibers as received (without no futher washing or treatment), definitely, diminishes the glass transition temperature of the composite as the excess of lubricant on the fibers exerts a plastifying effect in the polymer matrix.

PLASMA POLYMERISATION FOR MOLECULAR ENGINEERING OF CARBON FIBRE SURFACES FOR OPTIMISED COMPOSITES

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The mechanism of adhesion of carbon fibres to epoxy and related resins has long been in dispute. Because of the complexity of the surface chemistry and microporosity it is often argued that adhesion has little to do with functional groups present. Plasma polymerisation provides a technique for depositing a molecularly thin conformal coating with strong adhesion to the fibre. Since the microporosity of the surface can be concealed, any functionality incorporated into the film can be considered to be the principal adhesion mechanism. Thus significant progress will be shown which demonstrates a relationship between fibre surface chemistry and the micromechanics of carbon fibre composites. The retention of surface chemical functionalities has been studied as a function of the plasma parameters. In addition, hydrocarbon films were also employed to explore interfacial reactions in the absence of reactive surface species. The fragmentation test was employed to correlate the adhesion of these modified fibres to the micromechanics of single filament composites.

Keywords: plasma polymerisation; carbon fibre; molecular engineering; interfacial adhesion; fragmentation test.

Surface treatment and modifications of Natural fibres in polymer matrix for the development of wood substitute in Building constructions.

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The search for alternate Building Materials eq. wood substitute to conserve the natural Forest resources has assumed special significance in view of the Environmental Protection. Natural organic fibres e.g. sisal, Jute, Sunhemp which are available in abundance throughout the world when preteated leading to the surface modification can be embedded in Polymer Matrix to produce a wood substitute composite material suitable for wall panels, Roof coverings, Door Shutters for Building construction.

The present paper discusses the structure - property-performance relationship of sisal/Jute natural fibres and their characterisation for use in polymer matrix as reinforcement. In addition Surface Treatment and their modifications to improve the Bond and performance of these fibres in polymer matrix for the development of various composites as an alternate -to wood in wall panels, false ceiling, roof covering, Door shutters including their physical and mechanical properties have been reported. The use of Industrial wastes eq. Flyash and Red Mud as fillers were also investigated in order to impart certain properties to the composites besides making it cost effective in various Building applications.

From the rigorous analysis and testing carried out on these composites in the Laboratory and field, it was concluded that the surface treated and modified fibres embedded in flyash/Redmud admixed in polymer matrix provided an alternate to wood. The 3 mm thick Redmud /Flyash, fibres reinforced polymer panel gave equivalent flexural strength to 10mm plywood panel having neglegible moisture absorption and superior performance. Several applications in Building construction eq. panel, false ceiling, door shutters etc have been successfully demonstrated to various Government and public organisations and have met their apprvoal as wood substitute,thus minimising wood consumption for the protection of environment and forest.

SURFACE MODIFICATION OF UHMWPE FIBRES AND FILMS THROUGH PLASMA ETCHING OR PLASMA POLYMERIZATION

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Gel-spun ultra high molecular weight polyethylene (UHMWPE) fibres have properties that would be advantageous in composite materials but have found limited practical application. The significance of improved adhesion to composite behaviour may be less than expected when the fibre has poor compressive properties. In this research a spectrum of UHMWPE surfaces were produced. Both UHMWPE fibres and films (as-cast and drawn) were modified in a plasma reactor. In one series of experiments UHMWPE was etched in either nitrogen, oxygen or argon to produce more hydrophilic surfaces. Of the gases studied a nitrogen plasma produced the largest increase in wetting. The wetting improved both with increasing power and increasing treatment time. Exposure to an oxygen stream accelerated the process of aging seen in the decrease in wetting with exposure to atmospheric conditions. In another series of experiments films of more hydrophobic plasma polymers were deposited on UHMWPE. A significant decrease in wetting was found on deposition of plasma polymerized hexafluoropropylene and plasma polymerized ethylene. The wettability of the film decreased significantly on drawing and the low power plasmas were more effective in increasing the wettability of the drawn films. The changes in wetting after drawing and/or surface modification were related to the changes in surface chemistry and topography.

Session 3B

POSITRON ANNIHILATION IN POLYMERS AND COMPOSITES

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Positron annihilation spectroscopy is a new unique method to probe defects and free volume hole sizes and size distributions in polymers and polymer composites. When a positron is injected into a polymeric material it can annihilate directly with an electron or capture an electron and form a bound state, a positronium atom (Ps).

Ortho-Positronium (o-Ps), in which the spins of the positron and electron are parallel, has a lifetime of 142 ns in vacuum. In condensed matter the lifetime of o-Ps is considerably reduced, due to the fact that the positron in the Ps atom can pick off an electron with anti-parallel spin from the surrounding molecules, to annihilate with. The o-Ps are preferentially formed or trapped in holes or regions of low electron density and the lifetime is proportional to the size of the holes.

An overview of the development of the positron annihilation methods will be given and the possibilities to apply the technique to polymers and composites will be presented.

IN SITU NEAR-IR INTERPHASE CURE MONITORING OF MODEL POLYMER MATRIX COMPOSITE MATERIALS

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Very little work has been done to follow curing reactions of polymers using the near-infrared (near-IR) portion of the electromagnetic spectrum because of the weak nature of the bands in this region. In addition, the interphase in glass fiber reinforced composite materials has not been studied directly with IR based techniques due to difficulty in applying these techniques. To circumvent these problems, a specially designed low refractive index epoxy has been used to make model composite materials. In this case fiber-optic evanescent wave sensing can be used with a silica fiber to examine the interphase region.

The curing of a low refractive index epoxy adjacent silica fiber has been studied. The low refractive index epoxy is a fluorinated resin which is mixed with an amine based hardener. For this work, the mixture was heated to 120°C for 3 hours to achieve curing. The experiments were performed by removing the buffer and cladding from a 1 cm region of the fiber to create a sensing region. The epoxy/hardener mixture was placed in specially designed holder to cover the sensing region. Near-IR light is internally reflected in the fiber and a spectrum is recorded as a function of time and temperature of cure. The curing reaction was followed by examining three bands. Prior to curing there is a band at ~4925 cm⁻¹ which disappears quickly after the temperature reaches 100°C. As this band disappears, a band at ~4725 cm⁻¹ begins to appear. The final band change occurs for the band at ~4325 cm⁻¹ initially. As the mixture is heated, this band shifts to ~4350 cm⁻¹ by 100°C.

In addition to curing the epoxy, the holder was also designed such that the glass fiber/epoxy interphase could be strained. While these strain measurements have yet to yield conclusive results, the bands which are present after curing of the epoxy will be examined for changes in position, height and half-width caused by strain.

CHARACTERIZATION OF THE INTERPHASE IN TWARON ARAMID FIBER APPLICATIONS

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Twaron aramid fiber, due to its exceptional properties, is used as reinforcement in high performance composites, involving thermoset, thermoplastic and rubber matrix systems. However, the chemical inertia of the fiber surface and resulting poor adhesion of aramid to polymer matrix systems, necessitates an "adhesion activation" (AA) process prior to manufacturing the composite. This AA process consists of the application of an epoxy-containing finish to the fiber surface, and subsequent thermal treatment thereof.

In order to evaluate nanostructural origin of the macroscopic adhesion property, characterization of the interphase is required. This involves chemical as well as micro-mechanical analysis of the interphase region. An essential prerequisite for this approach is the use of well-defined starting materials, notably the fibre substrate. It will be shown that finishes, sizes and other essential processing components, as well as contaminants at the interphase, may exhibit a large effect on the intended surface modification process.

In this work, the practical fiber-matrix adhesion level, measured using a bundle pull-out test, will be correlated with the interphase structure. Moreover, the effect of surface modification (AA) process parameters on the resulting interphase structure will be demonstrated. To this end, commercial products and processes will be compared with model systems.

STUDY OF FIBRE SURFACE TREATMENTS FOR CONTROL OF INTERPHASE PROPERTIES IN COMPOSITES

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The paper presents results from a study of the fibre-matrix interaction and deals with the inter-relationship of fibre surface treatment, wetting behaviour, and interfacial strength.

Different matrix compatible and non-compatible glass fibre sizings and non-treated and surface treated carbon fibres were studied by XPS, IGC, Zetapotential, and wetting measurements with model liquids in previous work.

In this paper, the aim is to assess the information that can be obtained from dynamic wettability measurements performed using these surface characterized reinforcing fibres and real viscous resins and to combine the assessment with the determination of interfacial strength.

It has been found that the kind of fibre surface treatment and interaction with the matrix influences the wetting kinetics of sized glass fibres or treated carbon fibres and polymer melts or viscous resins.

The resulting interfacial strengths in selected fibre/matrix systems have been assessed in dependence on the wetting characteristics.

The experimental results of the single-fibre pull-out test show that the fibre-matrix interaction strongly depends on the chemical modification of the matrix as well as on the sizing. The experimental results of the modified Wilhelmy wetting method show that chemical reactions together with interdiffusion effects take place in the interphase and influence the wetting kinetics between surface treated fibres and polymer melts or resins. Differences in the wetting kinetics due to the size formulation were found to influence the interfacial strength.

FUNDAMENTAL STUDIES OF FIBERGLASS IN COMPOSITES

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ABSTRACT

Glass surface composition is the first building block of the "inter-phase," and it varies through changes in the parameters of fiber forming, as well as changes in the bulk oxides used. A wide range of surface chemistries is represented in the commercial compositions: E, AF, S-2 and the new bicomponent fiber, Miraflex (TM). XPS, zeta potential, and contact angle measurements are used to characterize the surface chemistry, electro-statics and thermodynamics, respectively. Those results are used to develop predictive relationships for wet-out, cure and adhesion of sizings and matrix resins to the fibers, as well as composite strength and durability. This overview will synthesize a coherent picture of the current state of the art by combining examples from the recent literature with new work from our laboratories and our collaborations with university and government labs.

Session 4A

Stress Analysis of the Fragmentation Test Including the Effect of an Imperfect Interface: Application to Interpretation of Experimental Results

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ABSTRACT

A new analysis for stress transfer from the matrix to a fragmented fiber through an imperfect interface was derived using a Bessel-Fourier series stress function with some important additional polynomial terms. The solution satisfies equilibrium and compatibility every place and satisfies most boundary conditions exactly. The only approximation is that the axial stress in the fiber at a fiber break is zero in an averaged sense instead of exactly. Two important advantages of the analysis are that it can handle anisotropic fibers and it can include imperfect interfaces or interphases.

The Bessel-Fourier series analysis will be used to discuss interpretation of fragmentation experiments. Some topics to cover are damage zones around fiber breaks and fracture mechanics predictions using energy release rate for fiber fracture or for debond growth. Finally, shear-lag analysis has been a popular tool for calculations on single fiber specimens. The Bessel-Fourier series analysis can be used to critically evaluate shear-lag methods as a tool for stress analysis.

SHEAR STRESS DISTRIBUTION IN THE FIBRE-MATRIX INTERFACE DURING LOAD TRANSFER

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ABSTRACT

Several test methods exist to determine the fibre/matrix interface strength (pull out-, push through-, fibre fragmentation-test, etc.), however one of the key problems is the estimation of the micromechanical shear stress at the point of debonding as a function of the applied load. This has yet not satisfactorily been resolved.

A micromechanical study of E glass/epoxy composite systems has been conducted by means of the fibre fragmentation test. For the matrix a Ciba-Geigy LY556®/HY932® epoxy resin, flexibilised with JEFFAMINE D2000® (Texaco), was used. E-glass fibres (diameter of 80 µm) uncoated and coated with aminosilan-, aminosilan + polymer dispersion- and aminosilan + epoxy dispersion-based sizings supplied, by IPF-Dresden, were used. For this purpose a special device was developed, which allows to in situ observe fibre fracture directly during loading via transmission light microscopy. The actual load-, respectively strain-distribution around a single fibre break can be estimated by quantitative photo elastic analysis. A representative isochromatic fringe pattern is shown in fig. 1. In addition to the experimental work finite element calculations of single fibre model composites were carried out.

To determine the interfacial shear strength distribution a model was developed based on the actual shear-lag theories, the finite element calculations and the experimental results. Our proposal to describe the interfacial shear stress distribution along the fibre as a function of the applied global load incorporates the influence of the viscoelastic behaviour of the epoxy matrix on the load transfer, the effect of matrix cracking, fibre/matrix debonding and the actual cumulative number of fibre breaks in the single fibre.

Furthermore there exist some hints that during the curing period a chain segregation occurs conditioned by the free surface energy difference and chemical reactions of the sizings with the epoxy matrix material. The consequence of the chain segregation can be the formation of a low modulus epoxy interphase. This low modulus interphase should influence the shear stress distribution along the fibre, but the occurrence of this interphase is not exactly clarified.

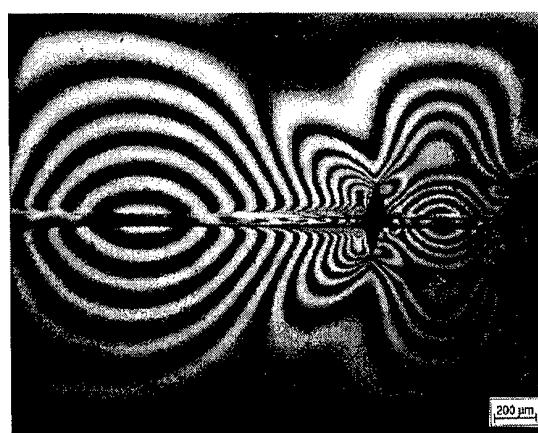


Fig. 1: Photo elastic fringe pattern. Single fibre coated with aminosilan based sizing. Applied stress 30.8 MPa.

THE ADHESIVE STRENGTH OF FIBER-MATRIX INTERFACE UPON
CYCLIC ACTION OF LOW TEMPERATURES.
THE EFFECT OF JOINT PREPARATION CONDITIONS.

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The success of reinforced plastics as engineering materials that can be exploited at low temperatures depends primarily on the strength of interface between the reinforcement and matrix. Because of this the effect of cyclic cooling from ambient temperature down to liquid nitrogen or helium temperatures on the shear adhesive strength (τ) of fiber - polymer joints was investigated by us recently. The thermosetting and thermoplastic matrices were examined. It was demonstrated that the multiple cooling produces loss of adhesive strength. The level of losses depends on the nature of components, on the cycle numbers, on the geometry of joints. The range of temperatures in which the specimens are cooled is also of significance.

It was concluded that the decrease of bondary strength is mainly determined by thermal residual stresses. These stresses depend significantly on the time - temperature conditions of specimen preparation.

Therefore in this work we study the influence of mentioned condition on the interface behaviour under repeated cooling down to liquid nitrogen temperature.

For this purpose the joints of epoxy composition EDT-10 and of poly(arylene sulphone) PSK-1 with high-strength steel wire of diameter 150 μm were tested by pull-out technique. This conditions of joint formation were as follows: 20 $^{\circ}\text{C}$ - 6 months; 160 $^{\circ}\text{C}$ - 8h.; 180 $^{\circ}\text{C}$ - 6h. - for epoxy joints; 300 $^{\circ}\text{C}$ - 0,5h.; 300 $^{\circ}\text{C}$ - 2h. - for poly (arylene sulphone) joints.

The data obtained show that initial fiber-polymer adhesive strength τ strongly depends on time-temperature regimes of specimen fabrication. These regimes control also the decrease of τ as a cycle number increases. They determine for example the number N of plunging into liquid nitrogen after which the losses of adhesive strength become noticeable.

Thus the level of interface strength in fiber-polymer systems and the level of interface strength losses after repeating cooling down to low temperatures depend on both - the nature of bonds and bond formation conditions.

This work is supported by International Science Foundation.

EFFECT OF INTERFACE UPON THE TENSILE FRACTURE OF UNIDIRECTIONAL COMPOSITES

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It has already been demonstrated that it is possible to measure both the interfacial shear capabilities and the stress concentration factors resulting from isolated fiber fractures in single, as well as, in full composites using the technique of laser Raman spectroscopy (LRS). This technique is based on the stress/strain dependence of the Raman vibrational frequencies of the reinforcing fibres (carbon, aramid, SiC, etc.), and can be applied to almost all fibre/ matrix systems provided that the matrix is reasonably transparent. Thus the highly sought link between single-fibre model composites and full composites, has been established.

The effect that a fibre fracture has upon neighbouring fibres has been studied in detail in (a) 2D microcomposites (b) standard tensile composite coupons and (c) fibre tows. The stress or strain along individual fibres at different levels of applied load has been monitored in an attempt to measure the transfer lengths , the stress-concentration factors and the positive affected lengths (PAL) in these composites. At each applied stress level, the interfacial shear stress (ISS) distribution was derived by means of a balance of shear-to-axial forces argument. In the single carbon fibre/ epoxy system, a maximum interfacial shear stress of 30 MPa was reached at the point of fibre first fracture. In the multi-fibre carbon fibre/epoxy system, the maximum interfacial shear stress developed at the point of first fibre fracture was of approximately the same magnitude. Finally, the local stress concentration in the intact fibres, as a result of an adjacent fibre fracture, was determined as a function of distance from an existing fibre fracture(s) for three distinct levels of applied stress.

A full review of existing models for the determination of the effect of the strength of the interface upon the fracture characteristics of unidirectional composites will be presented. The values of stress concentration obtained from the 2D microcomposites will be compared with analytical models based on planar fibre geometries. In addition, useful comparisons between the results obtained from the full composites and 3D analytical, as well as, FEA models will be made. Finally, the possibility of establishing a new approach based on the Raman results obtained from different geometries and material systems, will be discussed.

THE TOUGHNESS OF THE FIBER / MATRIX INTERFACE MEASURED BY THE SINGLE FIBRE PULL OUT TEST

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Abstract:

A new method for the experimental determination of the fracture toughness in the fiber / polymer matrix interface by means of the single fiber pull out test is presented. To achieve this aim, two problems had to be overcome: the measurement of the compliance of a partial debonded fiber, which necessitates a stable crack propagation, and the determination of the corresponding crack length.

Stable crack propagation along the interface of a single fiber is achieved using an advanced test equipment exhibiting an extremely high stiffness. This is obtained by using a piezo translator and a piezo force cell in combination with a very short free fiber length. The experimental data and a theoretical analysis of the pull out process under these conditions reveal, that the commonly used compliant pull out equipment is hiding important details of the force displacement trace and thus leading to a wrong interpretation and wrong results, i.e. in the case of a brittle interfacial failure:

- the rising part of the pull out trace exhibits two slopes
- the kink between these slopes is indicating the initiation of the crack
- the maximal force is only indicating the onset of unstable crack propagation
- the maximal force is dependent on the friction after debonding, the level of the crack initiating force and the onset of the unstable crack propagation.
- the crack initiating force is not a function of the embedded length in the case of a glass fiber. In the case of a carbon fiber with an embedded length < 150 μm it is a function.

The most important result is, that the maximal force cannot be used for the determination of an interfacial strength as it is common practise till now.

The crack length is measured with the aid of a polarisation microscope. A combination of the advanced pull out experiment with a simultaneous monitoring of the photoelastic patterns of the embedded fiber enables the determination of G_C - values as a function of the crack length. For the calculation of G_C the compliance data are obtained by the force displacement trace and the crack length data by the correlated photoelastic patterns. The discrimination between the failure modes is obtained by finite element analysis. The energy release rates for different fiber / matrix combinations are presented. In addition the photoelastic patterns give evidence, that in the case of a glass fiber the crack starts at the matrix surface and in the case of a carbon fiber with an embedded length < 150 μm the crack starts at the fiber tip.

The Effect of Moisture on the Relative Durability of both Glass Fibers and Fiber/Interfaces using the Single Fiber Fragmentation Test

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Moisture has the potential to attack fiber, resin, and the interfacial region in a polymer matrix composite. The goal of this work was to look at the relative durability of both the glass fiber and the interfacial region using the single fiber fragmentation test as a function of both type of glass fiber and time of exposure to water. The fragmentation profile of the fibers in the single-fiber dogbone showed that hydrothermal treatment in 75 C distilled water decreased the relative apparent strength of both the fiber and the effective interfacial shear strength. Differences existed between the fragmentation profiles for the E, ECR and S glass fibers, and degradation of both the strength of the fiber, sigma subf, and effective interfacial shear strength, tau, occurred. Relative rates of degradations of the glass were S < ECR <(less than or equal to) E, and these scaled with an increase in content of sodium. Inductively coupled plasma mass spectrometric (ICPMS) analyses of water in which the samples soaked showed the presence of leached ions unique to the types of glass fibers investigated: E (Ca, K, and Mg), ECR (Ca, K, and Mg) and S (Ca, Mg, Fe, and Ba). These analyses were consistent with mechanisms responsible for loss in strength of the glass including both leaching of ions and stress corrosion. Furthermore, water decreased the properties of the epoxy resin as well.

Session 4B

FRACTAL NATURE OF INTERFACES IN COMPOSITES:
OBSERVATION, CHARACTERIZATION, AND MECHANICAL IMPLICATIONS

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The fractal morphology of surfaces of advanced reinforcing fibers and its implications on composite micromechanics are addressed. Methods of fractal analysis of fiber surfaces are reviewed. Limitations of adsorption, SEM image analysis, and X-ray scattering are discussed. Advantages of atomic force microscopy (AFM) are elucidated. AFM observations of several graphite, polyaramid, and polyimide fibers are presented and analyzed. All fibers are found to possess self-similar fractal surfaces over a scale range from nanometers to microns. Methods of quantitative characterization of fractal surfaces by AFM are reviewed. The techniques covered include box counting, power spectrum, lake/island perimeter-area, structure function, and multiple image variography. The latter technique coupled with removal of global cylindrical curvature is found to be robust. This technique is applied to quantitative fractal characterization of AFM images. A roughness parameter, defined as the root-mean-square deviation from the mean plane, is estimated at different scales. Cylindrical curvature of the surface in the transverse direction is removed by the second order polynomial approximation. Roughness scaling exponents and fractal dimensions D of surfaces are estimated from the slopes of the log-log plots of roughness versus scale. Calculated fractal dimensions span the interval from 2.09 for commercial graphite T40R fiber to 2.52 for an undrawn experimental polyimide fiber. Deviation of D from an integer value of 2 is higher for polymer and lower for graphite fibers. The fractal dimension of the polyimide fibers decreases almost linearly from 2.52 for as spun, undrawn fibers to 2.18 for fibers with a draw ratio 8.

The fractal nature of the fiber surfaces implies that the interface regions in composites also have fractal morphology. A literature review on fractal interfaces shows that most studies deal with chemical (adsorption) or physical (phase transitions) phenomena in the vicinity of interfaces. Mechanical aspects of interactions at such interfaces are virtually uncovered. Fiber composites with fractal interfaces and a transitional layer (interphase) between the fibers and the matrix are analyzed in this paper. Micromechanics models for effective elastic, viscoelastic, and thermal properties of a unidirectional composite in longitudinal and transverse directions are developed. Variation of elastic and transport properties, expansion coefficients, viscoelastic loss and creep factors with the thickness of the transitional layer are analyzed for different fractal dimensions of the interface. Strong effects of the fractal dimension on effective mechanical properties are observed. Implications of the self-similar geometric morphology on fracture and damage mechanics of interfaces in composites are discussed. The importance of fractal characterization and design of interface regions in composites is emphasized.

CRYSTALLISATION ANALYSIS AT CARBON FIBRE / PEKK INTERFACES IN MODEL COMPOSITES

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The aim of the present study is to analyse the crystallisation behaviour in the vicinity of the fibre-matrix interface in model composites, constituted by PAN-based carbon fibres (oxidized T300 fibres, Soficar) embedded into poly(ether-ketone-ketone) (PEKK) semi-crystalline polymer. This polymer (Du Pont de Nemours, Germany) exhibits glass transition and melting temperatures of 149 and 301 °C respectively. Two main techniques were used to characterize its crystallinity in the bulk and near the carbon fibre surface : differential scanning calorimetry (DSC) (Mettler DSC 30) and microscopical Fourier transform infrared spectroscopy (FTIR) (Bruker IFS-66). Spectra were recorded, for the former, at a heating rate of 20°C/min and, for the latter, at a resolution of 2 cm⁻¹ using a beam diameter of 22 μm and by averaging 100 scans. Each sample, in the form of thin film (10-15 μm thick), was prepared into a Linkam THM 600 heated microscopical plate equipped with a temperature programme planner, enabling temperatures to be varied at adjustable heating and cooling rates. For model composites, a few carbon fibres were put prior to melting into two thin sheets of PEKK. Melting of polymer was first obtained by heating up at 380°C, for a dwell time of 10 min, then the following thermal treatments were carried out : (i) quenching, (ii) isothermal crystallisation at 200, 220 or 240 °C, for different times (up to 60 min), followed by quenching to room temperature, (iii) slow cooling from the melt to RT at 1°C/min. These thermal treatments strongly affect the degree of crystallinity of the bulk polymer as revealed by DSC, since its enthalpy of melting ΔH_m varies from about 0 for quenching to 30 J/g for slow cooling. Moreover, it appears that significant differences on infrared spectra can be observed between about 950 to 1000 cm⁻¹. In fact, a linear relationship can be established between ΔH_m and the optical density ratio A(999/987) of the infrared peaks at 999 and 987 cm⁻¹ respectively, indicating that this ratio is representative of the degree of crystallinity in the bulk polymer. Finally, by means of this relationship, it clearly appears that the degree of crystallinity is always higher in the vicinity of the carbon surface than in the bulk polymer, whatever the thermal treatment except the slow cooling procedure. For example, in the case of quenching, ΔH_m near the interface is equal to about 10 J/g instead of 0 in the bulk. Moreover, new infrared peaks of small intensity are observed in the range of 950 to 985 cm⁻¹. Nevertheless, it is impossible at present to attribute these peaks to a new type of crystals, for example to the growth of a transcrystalline layer, which is never observed near the fiber surface.

CONTRIBUTION OF CRYSTALLINITY ON THE INTERFACIAL STRENGTH IN THERMOPLASTIC COMPOSITES

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ABSTRACT

In the case of semicrystalline thermoplastic composite, the phenomenon of fiber/matrix adhesion has been widely discussed in terms of transcrystalline structure at the interface. Particularly in the case of polyetheretherketone/carbon fiber composite, some authors have suggested that the outstanding interfacial strength observed in the APC-2 (AS4/PEEK) composite is strongly related to the ability of the polyetheretherketone (PEEK) matrix to produce a transcrystalline layer around the carbon fibers. However, it has been shown that the high-strength AS4 fiber has a significantly lower nucleation tendency than the high-modulus HMS fiber, which easily generates transcrystallinity in PEEK but leads to very low transverse flexural strength compared to that of the AS4/PEEK composite. Previous works done in our laboratory on the optimization of processing of PEEK, polypropylene (PP) and polyamide (PA) carbon fiber composites have shown that the mechanism responsible for the creation of the interaction between the AS-4 carbon fiber and thermoplastic matrix is time-temperature dependent. The concept of adsorption was found to be valid for interpreting the evolution of the short beam shear strength with residence time, as described by a Langmuir-type expression. The temperature dependence of the formation of the fiber/matrix interaction, as measured by the short beam shear strength, is also found to follow an Arrhenius equation with an activation energy of about 324 kJ mol^{-1} for the PEEK/carbon system. The high value of the activation energy and the irreversibility of the interaction process suggested that chemisorption could be a dominant mechanism for the establishment of the fiber/matrix interaction.

In the present work, it is shown that although physicochemical mechanism seems to be the primary factor responsible for the creation of fiber/matrix interaction in thermoplastic/carbon fiber composites, interphase crystallinity is also essential to ensure optimum interfacial strength. However, it is well demonstrated that effect of interphase crystallinity on the interfacial strength is greatly related to the extent of fiber/matrix interaction. In case of PEEK and PA/carbon fiber composites characterized by strong physicochemical interactions, the interfacial strength seems to be related to the crystalline structure of the thermoplastic matrix. Changes in the evolution of the interfacial strength as a function of cooling rate during processing were found to correspond to changes of crystallization mechanism of the matrix. Low cooling rates leading to high level of crystallinity result in a significant increase of interfacial strength. In case of PP/carbon fiber composite, due to the low reactivity of its chemical structure, the fiber/matrix interaction was found to be low and the interfacial strength did not seem to be affected by change of interfacial crystallinity. These results suggest that contribution of interphase crystallinity to the interfacial strength is significant only when a strong physicochemical interaction between the fibers and the matrix has been created. Finally, non-coupled PP/glass fiber composite shows an opposite result; significant reduction of the interfacial strength for highly crystalline material is obtained. In this case, it is well known that the establishment of fiber/matrix interaction can be obtain only in presence of coupling agent or functionalized PP and without such additive only wetting force can contribute to the interfacial strength. Since wetting is favored in presence of amorphous phase the reduction of the interfacial strength for highly crystalline composite can be associated to the reduction of the amorphous phase.

**TAILORING THE INTERPHASES IN
CARBON OR GLASS-POLY(PHENYLENE SULFIDE)
SYSTEMS BY CONTROLLING
THE GROWTH OF TRANSCRYSTALLINE LAYERS
OR BY USING POLYMERIC CO-COUPLING AGENTS**

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Composite materials based on poly(phenylene sulfide) and carbon or glass fibers are promising materials according to their high temperature and chemical resistances. The interfacial regions need to be controlled to improve the mechanical properties in these composites due to the semi-crystalline nature of the PPS. In this paper, two different ways for controlling the interphases are investigated. Firstly, the approach is based on the ability of the PPS to form transcrystalline zones in the vicinity of the fiber surface. The influence of the presence of carbon fibers and of their surface treatments (oxidization, sizing), and the processing conditions are reported. The mechanical and fracture properties of unidirectional composites are studied as a function of the processing conditions. The fracture mechanisms can be related to the structure of the interphases. Secondly, a new concept is applied for tailoring the interphases for glass fibers/PPS composites by grafting the glass surface with polymer chains able to interdiffuse in the bulk matrix and to co-crystallize with it. The co-crystallization and the interfacial shear strength of the glass fiber/PPS (studied by means of the microbond test) are discussed as a function of the nature of the polymer chains, the type of functionalization (side chain or chain end positions), and the melting-crystallization conditions. The interfacial adhesion is greatly enhanced with the use of such functionalized co-coupling agents and this improvement is verified on short glass fibers-based composites.

Poster Session 2

STUDY ON WETTING BETWEEN GLASS FIBRES AND POLYPROPYLENE MELTS USING THE WILHELMY TECHNIQUE

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Abstract

A more fundamental and quantitative understanding of the mechanism for interphase formation in fibre reinforced polymer composites is needed to enable tailoring of the interphase. In the case of polypropylene-glass fibre composites, not only the glass fibres are surface-treated but also the non-polar polypropylene matrix itself has to be chemically modified with polar groups to ensure efficient stress transfer between fibre and matrix.

We used wetting measurements between individual glass fibres and polypropylene melts as a model system to study thermodynamic and kinetic processes under conditions comparable to processing conditions of the composites. The results of these measurements should provide direct informations about the driving forces for interphase formation in these systems. Generally, these experiments are difficult to carry out because of high measuring temperatures, high viscosity and limited thermostability of the polymer melts.

A high temperature apparatus was developed to determine the surface tension of the polymer melts and their wetting kinetics on fibre surfaces up to temperatures of 500° C in defined environment (vacuum or inert gas). As measuring principle the Wilhelmy technique is used. A very sensitive electrobalance records the force exerted on the fibre after it was immersed in the polymer melt at a certain temperature. The high temperature cell is equipped with two windows which allow the imaging of the fibre while immersing into the melt by a CCD camera on a video monitor.

Experimental results are presented for a series of sized glass fibres consisting of incompatible and compatible sizings in contact with unmodified and chemically modified polymer melts. Additionally, the acid-base properties of the fibre surfaces were characterized by zeta potential measurements in electrolyte solutions with varying pH. Thus, the effects of different sizings with known acid-base characteristics could be quantified by measuring the wetting tension of the polymer melt on the fibre surface as a function of time at temperatures above 200° C.

The type of wetting kinetics enabled us to distinguish between physical interactions at the fibre-polymer melt interface and specific interactions probably acid-base interactions and interdiffusion effects due to different sizing formulations and the presence of reactive groups in the polypropylene.

EMBEDDED SINGLE FIBRE DYNAMIC LOAD TEST AS A METHOD FOR INTERPHASE CHARACTERIZATION

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Tests on embedded single fibres are usually used to investigate the adhesion between fibre and matrix. Therefore in the last years single-fibre pull-out and single-fibre-fragmentation methods were developed to get experimental specifications about fibre-matrix interactions in brittle and ductile systems, especially about damage characteristics. However, the interpretations of the results of these experiments are complicated by the instable crack propagation. Most of the applied theories use an energy or stress analysis to deduce the interphase properties from received results indirectly.

As a further development, based on the single-fibre pull-out test, an apparatus for dynamic load test is built up in Institute of Polymer Research, to determine the interphase properties by a nondestructive method.

Specimens with a small free fibre length of 2 up to 5 times of the diameter of the fibre have been used. The specimen has been loaded by sinus vibrations of a piezotransducer in a pull and push mode with an amplitude of $1\mu\text{m}$ and a frequency of 1 up to 100 Hz. These vibrations end up in stress waves of 10 up to 40 mN, depending on the material properties.

By application of a special algorithm, which bases on the fourier transformation, the phase displacement or the damping $\tan \delta$ can be determined. The temperature has been varied from room temperature up to approximately 300°C , to characterize the glass transition of the polymers.

The goal of the tests is, to get information about the influence of modified surfaces and interphases on the modifications of the structure in composites.

The method of the dynamic load test bases on the hypothesis, that the fibre-matrix interphase is locally loaded by the moving fibre, whereas the distant matrix is lesser involved. Especially the FEM-results show that stresses caused by the fibre load are inversely proportional to the radial distance of the fibre. On the other hand the stretching of the interphase is in the linear-elastic region and not nearly as high that it could damage. So $\tan \delta$ might be a measure of the conditions of the interphase.

In this paper first experimental results should be presented. The structure and the experimental details of dynamic-load-test apparatus should be displayed. The paper should give information about the influence of the temperature on the plastic properties of the interface in different composites.

Basing on first results the poster should give a future outlook on the possibilities of characterising interfaces, offered by this dynamic-load method .

Polymers grafted cationically on silica surfaces

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To improve the adsorption between an inorganic material and an organic polymer special coupling agents are used.

The cationic vinyl polymerization in the presence of Lewis acceptor surfaces (cationic interfacial polymerization) shows a new route to form composites of inorganic solids and organic polymers [1], [2].

The synthetic principle of cationic interfacial polymerizations has been described in detail [2], [3]. However, the knowledge of the nature of grafted insoluble polymers fixed on the silica surface and the types of their chemical bonds are largely unknown.

Surface sensitive X-ray photoelectron spectroscopy, IR spectroscopy and electrokinetic methods have been used to characterize the surface regions and to evaluate the surface properties of poly(furfuryl alcohol) silica and poly(cyclopentadiene) silica composites.

It has been found that the cationically grafting of furfuryl alcohol on silica runs preferably as a polycondensation reaction by removing of alcohol groups. In contrast, cyclopentadiene undergoes a polymerization reaction by opening of double bonds.

All investigated composites shown stable covalent Si-O-C-bonds. Furthermore various new functional groups have been detected and could be specified by labelling reactions. Electrokinetic investigations have shown that the insoluble grafted polymers partially shield the acceptor centres of the silica surface, and a strong change of the surface properties have been observed.

The presence of functional surface groups enhances the synthetic potential of the formed composites, consequently it should be possible to generate surfaces highly suitable for a lot of applications.

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Dielectric investigations on HDPE/CaCO₃ compounds - structures of the interfaces

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The dielectric behaviour of a heterogeneous material, such as HDPE/CaCO₃ is described through the components DK and polarisation effect on the boundary surface. The DK for HDPE/CaCO₃ composite with $\epsilon_{\text{CaCO}_3} = 2,2$ and $\epsilon_{\text{CaCO}_3} = 8,0$ was calculated in dependence from the degree of filling, based on Bruggeman relation. Comparison of the relation obtained with values measured for stearic acid (STS) modified HDPE/CaCO₃-STS composite, shows a good agreement between them. Differences in the stearic acid content of the composite does not manifest in the DK-values, since this content is very small ($C_{\text{STS}} \ll C_{\text{PE}}, C_{\text{CaCO}_3}$), corresponding to no differences in the DK-values ($\epsilon_{\text{CaCO}_3} \approx \epsilon_{\text{STS}}$). Thus, it indicates that no declaration about the distribution of the modifier in the composite can be made by this way. It is possible to extract information's through the use of water as dipole measuring point at the boundary surface. A water adsorption and - desorption behaviour was observed at the boundary surface after carrying out a soaking and drying treatment of the composite, respectively. A pre- treatment of the filler material with hydrophobic modifiers reduces the water adsorption and also with it, the ion concentration at the boundary surface. Through the studies on dielectrics (dipole measuring points: water and/or aceton) it is possible to find the difference in the boundary layers of HDPE/CaCO₃ composites, having different degrees of modification. It has been found that there exist different structures of the interfaces, depending from the stearic acid or isopropyltriisostearic acid content of the composite. The maximum of interaction between the polymer and filler material corresponds to a concentration of the modifier covering partially the surface area. Furthermore, it is found that with an increasing modifier content of the composite, there is a complete covering of the interface. The YEH model can be proposed for the description of the interface structure.

REINFORCEMENT OF ELASTIC MODULUS IN ULTRAFINE PARTICLE FILLED POLYMERS

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It is known that the interface phenomena in heterogeneous polymeric materials strongly depends on the particle size of inorganic or metallic filler.

Now a new method of preparation of polymer composites has been elaborated. The method leads to a very uniform microscopic dispersion of colloidal particles in polymer matrices [1], i.e. comparatively uniform polymer-metal cluster composites can be obtained

The presence of such metallic microscopic clusters in polymer matrices has been investigated in many ways, e.g. by measurements of their optical properties. In this paper we want to discuss the influence of metal clusters in polymer matrix on some its mechanical properties, namely the reinforcement of elastic modulus in ultrafine particle filled polymers. As an example a polymethyl-metacrylate (PMMA) palladium-cluster composite will be discussed.

The method of preparation of the composites is similar to that described by Nakao [1]. The elastic modulus was measured as a function of palladium contents which never exceeded 0.010% volume fraction. The diameter of metal cluster was about 20 Å. The elastic modulus of the palladium cluster composite was about 5 times as great as the modulus of the pure PMMA.

Discussion of the relative modulus E_c/E_1 (where E_c the modulus of the composite and E_1 is the modulus of the matrix) shows that the model considering perfect particle binding and formation of dense polymer chain network surrounding the fine filler particles may be very useful for interpretation of the results. Considering the classical analysis of these multiphase structures one can show that such singularity like the detected increase of the modulus for the very low filling degree with metallic cluster particles can be explained in a consistent way.

Similar results were found when other metallic clusters have been used as very low content fillers in various amorphous polymers.

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A NOVEL SINGLE POLYMER COMPOSITE MATERIAL CONSISTING OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE FIBERS AND MATRIX

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Ultra-high molecular weight polyethylene (UHMWPE) has advantageous properties for advanced applications. Ultra drawn fibers based on this polymer (e.g. Spectra®) have outstanding mechanical properties. Successful utilization of polyethylene (PE) as a matrix material has so far been limited to low- or high-density PE jointly with surface chemical treatment of the reinforcing UHMWPE fibers. Furthermore an outstanding problem with PE/PE composites is the low adhesion of PE matrix to UHMWPE fibers.

We report a method for fabricating a composite material in which a matrix of UHMWPE is utilized with ultra drawn UHMWPE fibers. The solution-based process also induces formation of an interphase layer in which molecules from matrix and fiber surface are reciprocally entangled. We believe that our novel composite material can combine the unique properties of high-performance UHMWPE fibers and the bulk UHMWPE matrix. The novel material can be tailor made in a wide range of properties: from materials for ballistic protection purposes up to ultra-light construction composite elements and winding wares. Preliminary results show good mechanical properties of the novel composite material. For example, a unidirectional composite sample, containing 73% Spectra-1000 fibers in a matrix of UHMWPE (~3,000,000 Da) exhibits:

shear strength ~ 25 MPa;

longitudinal tensile strength ~ 1500 MPa;

transversal tensile strength (for non-molded sample) ~ 23 MPa;

longitudinal elongation at break ~ 2%;

transversal elongation at break (at 25 °C, non-molded sample) ~ 70%.

This non-molded composite may be subjected to further molding by compression or calendering to desired shape and properties. A particular advantage is the possibility of attaining orientation of the matrix in different directions.

**WEIGHT CHANGE ANALYSIS OF THE INTERPHASE
IN HYDROTHERMAL AGED FRP
- CONSIDERATION OF DEBONDING -**

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During immersion of fiber reinforced plastics (FRP) in water environment, significant debonding often appears between fiber and matrix, and it greatly affects the weight change kinetics of FRP. Therefore it is important to evaluate the effect of the debonding at the interphase on the weight change behavior of hydrothermal aged FRP. This study proposes the appropriate evaluation method of weight change in hydrothermal aged FRP in consideration of debonding between fiber and matrix.

Material used in this study was randomly oriented E-glass fiber continuous strand mat reinforced vinylester panel, and it was immersed in hot water at 95°C for predetermined immersion time. In the experimental approach, the weight change was evaluated by two parameters, weight gain due to water absorption (M_g) and weight loss due to dissolution (M_l), which were given by;

$$M_g = \frac{W_w - W_d}{W_o} \quad M_l = \frac{W_o - W_d}{W_o}.$$

where W_o and W_d were the weight of the dry specimen before and after immersion, and W_w was the weight of the wet specimen after immersion. M_g at short immersion time showed the typical Fickian diffusion behavior and was induced by only the water absorption of the matrix resin. In this process M_l was equal to zero and the degradation of the interphase never occurred. As the immersion time was longer, M_g showed the non-Fickian diffusion and it continued increasing. Simultaneously M_l also increased in the non-Fickian diffusion process. At the longer immersion time the water reached at the interphase region, and as a result, the interphase absorbed the water. Such water induced the degradation of the interphase, and dissolution of the components at the interphase such as silane coupling agent and binder was caused by the absorbed water. As a results of the dissolution, the weight of the whole material reduced significantly, and the debondings between fiber and matrix were produced. In this process the water penetrated into the debonded interphase and it led to the marked increase of M_g (non-Fickian diffusion). From these facts, the influence of the debonding at the interphase must be considered in the analytical approach for the weight change kinetics.

The weight gain at short immersion time can be obtained by the traditional diffusion analysis since the weight change was induced by only the water absorption of the matrix. Therefore the scope of this study was the analysis of the weight gain at long immersion time. At long immersion time the crescent-shaped debonding was observed microscopically in aged FRP. Therefore the marked increase of the weight gain was induced by the penetration of water into the debonded area. In other words, it was induced by the replacement of the component at the interphase to the environmental water. Hence, the weight gain due to this phenomenon (M_{gI}) was obtained by;

$$M_{gI} = M_l' \times \frac{\gamma_w}{\gamma_d}$$

where γ_w and γ_d were the densities of the water and the component at the interphase (mainly binder). M_l' was equivalent to M_l , however, it was calculated from the microscopic observation of the size of the crescent-shaped debonding. In our poster, the calculation method of M_l' and the analytical results obtained by using this method will be presented.

EFFECTS OF THERMAL TREATMENTS ON THE INTERFACIAL SHEAR STRENGTH OF NYLON 6 - GLASS AND CARBON FIBER COMPOSITES

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The overall mechanical behaviour of a composite material depends on the properties of the matrix and the reinforcing elements and on the independent behaviour of the fiber-matrix interface. For the optimization of a composite mechanical property, therefore, the effect of processing conditions on both the matrix properties and the fiber/matrix adhesion must be well evaluated. Thermoplastic polymers based composites present undoubted advantages in terms of processing, handling, damage tolerance, environmental resistance, recycling, and toughness. As for most thermoplastic polymers, mechanical and thermal treatments can induce structural changes in the matrix which will strongly affect composite mechanical properties. Recently it has been reported the effect of in vacuum thermal treatments on structure, molar mass, tensile modulus and strength of nylon-6 fibers [1]. Similar behaviour was also exhibited from thicker specimen (1.6 to 3.2 mm) of nylon-6 and its composites with short glass fibers [2]. In particular, a pronounced increase of the tensile modulus and strength of nylon-6 reinforced up to 50 % by wt. of glass fibers was measured. The improvement of interface between matrix and reinforcement could be assumed to be the reason of the reported results.

This paper presents results of the study of the effects of vacuum thermal treatments on the fiber-matrix interfacial adhesion in nylon-6 reinforced with glass and carbon fibers. The interfacial shear strength has been evaluated through the fragmentation test [3] performed on single fiber micromposites obtained by carefully sandwiching parallel individual monofilaments between two rectangles of dried as received nylon-6 films. Glass and carbon fibers with various commercial sizings have been used.

Vacuum thermal treatment at 190 °C for 48 hours resulted in a strongly increase of the interfacial shear strength for all the fibers we have tested. This effect was particularly marked for the unsized glass fibers whose interfacial shear strength raised from 19 MPa to 42 MPa as a consequence of the thermal treatment. A correspondent strong increase of the matrix crystallinity content and of the average viscosimetric molar mass have also been measured. The better interfacial shear stress transmission of treated composites could be explained by considering the higher mechanical properties of the bulk matrix and the interfacial region. Further experimental observations are in progress, in order to investigate the possible presence of a transcrystalline layer due to the thermal treatment.

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ADHESION STRENGTH OF FIBROUS COMPOSITE: ANALYTICAL STUDY AND COMPARISON WITH EXPERIMENTS

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Experimental evaluation of the adhesion strength in the case of fibrous composite may be founded on the basis of the solution of a complicated mechanical problem concerning the distribution of contact stresses between the fibber and matrix in the presence of a crack on the interface. Its rigorous consideration on the level of the composite components meets essential difficulties. Therefore, numerical and crude analytical approaches are widely used. In such studies singular behavior of the contact stresses is not taken into account and adhesion strength turns out to be dependent on the geometric parameters of the adhesive joint.

In this connection an asymptotic approximation to the problem under consideration was developed which enables to account a real stress singularity. On this basis the adhesion strength is estimated as a unique characteristic of a given adhesive pair. Comparison with experimental results confirms this point.

ON THE TRANSITION BETWEEN MICROHOMOGENEOUS AND CRAZE-LIKE MECHANISMS OF DEBONDING IN PARTICULATE COMPOSITES

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The experimental study of particulate filled polyolefines uniaxial deformation revealed two different modes of phases exfoliation. The first one is the independent debonding of different particles and takes place at the low filler fraction when the interparticle interaction may be neglected. The characteristic feature of the second way is the formation of narrow zones with completely debonded inclusions transversally oriented to the direction of the drawing. It occurs at rather high filler content when interparticle interaction is noticeable.

As it was shown by the mentioned study debonding mechanism is very important for regularities of further plastic deformation and fracture. It determines ductile or brittle fracture, macrohomogeneous flow or deformation with necking etc.

The subject of the present representation is theoretical explanation of the phenomena in frameworks of linear elastic constitutive equations. The process of uniaxial tension is supposed to be accompanied by the partial debonding in accordance to the energy balance between the energy storaged and its loss by the way of new surface formation. The model predicts certain mechanism of debonding and transition between them with the increase of filler fraction. The transition point is shifted to the right with the increase of the width of particles size distribution.

The conclusions of the model are in qualitative agreement with experimental data.

DEFORMATION MICROMECHANICS IN POLYETHYLENE/EPOXY COMPOSITES USING RAMAN SPECTROSCOPY

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Over the last decade, very strong emphasis has been given to the interface between the reinforcing fibre and the matrix as the controlling region for stress transfer between them. A lot of work has been done in this field leading to the conclusion that the composite performance depends heavily on the interface, but very little is known about how it actually works.

The analysis of model composites using Raman Spectroscopy opens the possibility of studying not only the reinforcing process, but also the failure of the interface by measuring *in situ* the stress or strain profiles that develop along the reinforcing fibre when the matrix is deformed.

Gel-Spun Polyethylene fibres are not only light weight but are also manufactured with an impressive levels of stiffness and strength which makes them very attractive as reinforcement for composites. In the case of Polyethylene/Epoxy Composites, the interface is particularly special. Firstly, it is formed by the interaction of a Thermoplastic with a Thermoset; secondly, it is rather weak due to the fact that polyethylene is a very inert material and thirdly, the fibre exhibits strong viscoelastic behaviour. The presentation will be concerned with the study of these factors using model composites. The interface was manipulated by changing the chemistry of the fibre surface or by post-curing the matrix, and its response to deformation and subsequent breakdown was mapped with Raman Spectroscopy. It was found that rather than the traditional stress transfer, in which the controlling factor is the Interfacial Shear Stress, the energy required to produce and propagate a Mode II Crack along the fibre/matrix interface, plus the friction generated by the irregular geometry of the fibre control the reinforcing and debonding process.

FRACTOGRAPHY OF FRACTURE ASPECTS IN CFRP

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ABSTRACT

In Fiber Reinforced Plastics (FRP) fiber is commonly treated by surface treatment to improve adhesion between fiber and resin. Effect of surface treatment is very important for material design. In the case of CFRP, oxidation and sizing are included among the surface treatment of carbon fiber. Mechanical properties of CFRP interface/interphase were investigated with various test methods, for example, single filament embedded tensile test, short beam test and so on. Fractography can be often used to understand for not only fracture behavior but also interfacial properties. In this study the fractography of CFRP from well defined experiments was performed, in which the detail of surface treatments could be presented in public. Materials used in this study were PAN based high strength type, high modulus type and pitch based high modulus type carbon fibers as reinforcement, a bis phenol-A epoxy type resin as matrix resin. These carbon fibers were subjected to continuous anodic oxidation in a 0.2 N aqueous solution of NH₄HCO₃ under electrical charge from 0 to 170 C/m². Epoxy type sizing agent was treated on those fibers by 50 % emulsion of bis phenol-A / epichlorohidrin.

In single filament embedded tensile test, interfacial transmissibility (**K**) was used as index of adhesion in interphase. In the case of PAN based high strength type, when interfacial transmissibility indicated **K**<0.2 and **K**=0.629, these filaments were pulled out from the resin, however, the resin adhered on the surface of these filament in the case of in higher **K** value. When **K** indicates 0.608, the filament was not pulled out from resin with mirror-zone. In the case of PAN based high modulus type carbon fiber, these filaments (**K**<0.2) was pulled out from the resin, and adhered resin was not observed on the surface of filament.

In the case of short beam test, ILSS increases with surface oxidation in each fiber. ILSS of PAN based high strength type seemed to be saturated the upper limit at electricity of 30 C/m². However large increase of ILSS by sizing treatment could not be seen. When fibers were treated with different concentration of sizing agent, fracture surface of those specimens were very similar to each other. Then it is consider that fracture aspects showed similar aspects when ILSS did not change. We could also report about transverse bending test and transverse tensile test of CFRP.

DELAMINATION BEHAVIOR OF GLASS WOVEN FABRIC COMPOSITES UNDER MODE I LOADING

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ABSTRACT

Proper design of the interface between fiber and matrix is necessary for tailoring the mechanical properties of composite materials. Interface or interphase in composite materials has been more important to understand various properties of composite materials and to develop new composite materials. Therefore, the most attractive issue in composite fields is how the micro structure on the fiber, i.e. interface, affects the macro scale properties of composite materials. Once micro-macro interaction would be clarified, the design of the interface could be also achieved.

One of our targets to design the interface is to identify the influences of the interfacial properties on crack growth behavior of composite materials. In this study, mode I interlaminar fracture toughness tests were carried out with glass plain / satin woven fabric vinylester composites with different interfacial properties. Mode I delamination behavior of the woven fabric composites was influenced by both interfacial properties and weave structure. Namely, the delamination behavior changed from stable to unstable manner with increasing concentration of silane coupling agent and with decreasing the number of transverse fiber strand to crack growth direction.

The objective of this work is to identify the relation between microscopic interfacial properties and macroscopic crack growth behavior of the glass woven fabric composites, especially unstable crack growth behavior. The unstable fracture occurs, when the release rate of stored energy is more than required for stable crack growth growth. This is attributed to interfacial properties and weave structure. The weave structure mainly cause bending cracks on the transverse fiber strand.

The effects of bending cracks have been investigated in order to identify the only interfacial effects on crack growth behavior of the woven fabric composites. Finite Element Method (FEM) analysis was conducted by considering the bending cracks. In the FEM analysis, the effects of the angle of the bending cracks have been discussed on the local fracture toughness.

The contribution of interfacial properties to the total fracture toughness of the woven fabric composites have been also investigated on the basis of the fractographic observation of mode I fracture surface. The total fracture toughness of the glass woven fabric vinylester composites is divided into the contributions from interface, resin and crack bending on the longitudinal and transverse fiber strands by considering crack path and weaving density.

EVALUATION OF FIBER/RESIN INTERFACE INSIDE OF FIBER BUNDLES

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ABSTRACT

Properties of interface in glass fiber reinforced plastics (GFRP) are important for decision of mechanical properties of GFRP. Various evaluation methods for interface in composite materials have been proposed such as single filament embedded tensile test, pull out test, push out test and so on. Interface in composite materials is consider to be mainly divided into four types such as pure interface between filament/matrix, fiber bundle interface between filament/matrix, crossing interface between two fibers which often appeared in woven fabric composites and laminar interface in laminated composites among them. The fiber bundle interface was focused in this investigation. Basically it is an idea to evaluate mechanical properties of interphase in fiber bundle by crack propagation inside of fiber bundle. The evaluation method for the fiber bundle interface has been investigated.

Materials used in this study were E-glass fiber as reinforcement and bisphenol -A epoxy resin as matrix resin. These glass fibers were treated with different concentration of APS silane coupling agent, 0wt%, 0.1wt%, 0.5wt% and 1.0wt%. Mode II fracture toughness tests were carried out using special End Notched Flexure (ENF) specimens whose shape was like a cylindrical rod. Initial crack was introduced into between filaments in fiber bundles by using fine cutter.

Initial values of Mode II fracture toughness, G_{IIc} , increased with increase of APS concentration. Transverse cross section and mode II fracture surface were observed by using scanning electron microscopy (SEM). In the transverse cross section, aspects of crack were different and divided roughly into two types. In the case of 0wt%, 0.1wt% and 0.5wt%, the crack propagated around filaments. On the other hand, in the case of 1.0 wt %, the crack propagates into filament/resin interface region between filaments. In the case of fracture surface, amount of resin adhered on the fiber surface increased with increase of APS concentration from 0 to 0.5wt%. It can be noted that G_{IIc} was related to amount of resin adhered on fiber surface.

DIACETYLENE CONTAINING URETHANE COPOLYMERS FOR STRAIN MEASUREMENT APPLICATIONS IN GLASS FIBRE COMPOSITES

by

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A variety of diacetylene containing urethane copolymers, based on 4,4'-diphenylmethane diisocyanate (MDI) and a hydroxyl-group terminated polypropylene glycol (PPG-400), using 2,4-hexadiyne-1,6-diol (HDD) to introduce diacetylene units, have been synthesized. It has been known that they have well defined Raman spectra. In this study, the thermal properties have been characterised by Differential Scanning Calorimetry (DSC) in relation to diacetylene composition. The diacetylene containing urethane copolymers are being used as coatings on the surfaces of glass fibres. The cross-polymerisation is carried out by heat annealing. They are shown to have well defined spectra similar as those of a polydiacetylene. The vibrational frequencies of certain main-chain Raman-active modes of the copolymer are sensitive to deformation which enables strain measurement to be undertaken by following the shift in the Raman band positions. It is shown that the peak position of the 2090 cm^{-1} band, which corresponds to the carbon triple bond stretching mode of the coated glass fibre, shifts to lower frequency under the action of tensile stress or strain as in the polydiacetylene itself.

This strain-induced band shifts of the polydiacetylene containing urethane copolymer coating can be used to map the distributions of stress or strain along the interfaces of glass fibres inside an epoxy resin matrix from which the interfacial shear stress can be calculated. It is found that the fragmentation of the glass fibre in an epoxy resin matrix can be studied and the strength of the interfaces in glass fibre epoxy composites analysed.

It had previously been thought that it was not possible to use Raman spectroscopy to follow deformation micromechanics in glass fibre reinforced composites but the results of this study have demonstrated that it can be done successfully though the use of diacetylene containing copolymer coatings on the fibres.

ON THE THERMODYNAMIC DEFINITION OF SURFACE STRESS

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Surface energy, surface tension and surface stress in a solid have been thoroughly discussed in literature. However, widely accepted definition of surface stress as the strain derivative of the *total* free surface energy divided by the surface area [Shuttleworth (1950)¹, Herring (1953), Zangwill (1988), Needs (1991), Cammarata (1992), Chou (1993), Wolf (1993), etc.] is inconsistent to the correct definition of a stress tensor (given in continuum elasticity theory²) as the strain derivative of the *specific* free energy. We analyze this incorrectness in details to prevent the erroneous use of the surface stress definition.

The definition of the surface tension in a solid requires to take into account the stress system as a whole in a surface layer of finite thickness (as distinct from liquids).³ In this work the surface tension has been represented in an integral form through a stress deviator distribution in a surface layer. This expression, applied to phases coexisting on both sides of the discontinuity surface, indeed gives the surface tension value, because integration limits may be changed to $[-\infty, +\infty]$. This is done taking into account that the inhomogeneity distribution in the surface layer is, in general, of asymptotic character.

The supposed general definition of the surface tension is valid for the particular cases of uniform and non-uniform solids and liquids. The expression that characterizes the relation between the surface tension of a homogeneous solid and the specific free surface energy referred to an element of a surface layer of finite thickness resting upon a unit surface area, has been obtained.

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MOISTURE ABSORPTION AND AGEING OF INTERFACES IN EPOXY MATRIX COMPOSITES

by

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Raman spectroscopy can be used to study the deformation micromechanics of a wide range of polymer, ceramic and carbon fibres in model, single-fibre composites with transparent resin matrices. By monitoring the peak position of strain-sensitive Raman bands it is possible to follow the axial deformation of the fibres in order to define the states of localised stress or strain in the composite matrix. The interfacial shear stress can be calculated from the distribution of axial strain along the fibre using a balance of forces argument.

The presentation will be concerned with the use of Raman spectroscopy to determine the effect of moisture absorption upon the point-to-point distribution of fibre strain for single-fibre model composite specimens and for different fibre surface pretreatments. The measurements have been undertaken using a cold-cured epoxy resin matrix immersed for various periods of time in distilled water at room temperature. Moisture absorption in an epoxy resin leads to significant matrix swelling. In the case of fibre-reinforced composites, if the fibre is unaffected by the moisture, matrix swelling leads to the build up of axial tensile strains in the reinforcing fibres. It has been demonstrated that Raman spectroscopy is an excellent technique to measure axial fibre strains resulting from matrix swelling for a variety of reinforcing fibres. Moreover it is possible using the technique to monitor the onset of interfacial failure as a result of moisture uptake.

Systems studied include aramid fibres with a variety of surface pretreatments, and alumina ceramic fibres, in the same epoxy resin matrix. Two geometries have been employed; the single-fibre pull-out specimen and the fully embedded single-fibre fragmentation specimen. The potential of the technique to monitor swelling in matrix materials and determine diffusion coefficients will be discussed. Furthermore it will be shown how it is possible to monitor progressive degradation of the interface due to the action of the environment.

THE EFFECT OF THE SURFACE MORPHNOLOGY, NETWORK STRUCTURE AND CHEMICAL MODIFICATION OF VULCANIZED SCRAP RUBBER POWDER ON THE PERFORMANCE OF THE TIRE TREAD

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ABSTRACT

To research character of surface morphnology, surface groups and interface between powder and natural rubber by kinds of tests, natural rubber and styrene-butadiene rubber which are usually used in the formulations of the tire tread and different vulcanization systems were chosed for the preparation of the vulcanize power with two kinds of methods in the lab. and then their powder was used to compare with the vulcanized scrap rubber powder made in the factory.

The results from SEM. showed that various powder particles had two kinds of forms: one was honeycomb-like, another was angular. There were lots of holes on their surface. The size and depth of holes mainly depended on different broken methods. It was indicated from infrared specturm that there were defect and few groups on the surface of powder after repeatedly crushed. It was evident from studying polt of swelling degree that carbon gel was not fully broken in course of vulcanize being comminuted. It still contributed to the network of powder. When unmodified powder belended with natural rubber, the interface compatibility was poor.

INFLUENCE OF SURFACE TREATMENT ON
MECHANICAL PROPERTIES AND CRYSTALLIZATION OF
GF/PP FILM STACKING COMPOSITES

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Long fiber reinforced PP composites (GF/PP) are of particular interest to different application fields, because of high impact properties, high stiffness, fast molding cycles, and reusability. It is well-known that these properties are influenced by surface treatment on glass fiber. In this study, unidirectional GF/PP composites were fabricated using film stacking method. Bending tests and mode I intralaminar fracture toughness tests were carried out to investigate the influence of surface treatment on mechanical properties. SEM observations were performed on fracture surface to discuss the contribution of surface treatment to the interfacial properties.

E-glass fiber treated with silane coupling agent and PP binder was employed as reinforcement. There were two surface treatment series called H series and SC series. In H series, amount of silane coupling agent was constant, and concentration of binder was changed. In SC series, amount of PP binder was constant, and concentration of silane coupling agent was changed. Both silane coupling effects and binder effects have been investigated in this study.

Three-point Bending tests were carried out and Mode I intralaminar fracture toughness tests were carried out by using special double cantilever beam (DCB) specimen.

In H series, both bending strength and Mode I intralaminar fracture toughness increased with increasing concentration of binder, and the amount of resin which was observed on the fracture surface increased with increasing concentration of binder. In SC series, bending strength and Mode I intralaminar fracture toughness displayed maximum value in medium concentration of silane coupling agent. The mechanical properties of GF/PP composites were correlated to the amount of resin adhered on the fracture surface. Therefore there is a optimum amount of silane coupling agent.

Moreover, crystallization morphology of the PP matrix on the interface was studied by polarized light microscopy, and relation between crystallization morphology and mechanical properties have been investigated.

INTERACTIONS BETWEEN NEIGHBOURING FIBRES IN MULTI-FIBRE COMPOSITES: THE PRESENCE OF MATRIX CRACKS

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It is now well established that the fibre/matrix interface plays a large role in determining the properties of a composite material. The majority of work on the interface has been performed on either bulk composites where it is difficult to isolate the effect of the interface, or single fibre model composites. The latter enables improvements in interfacial adhesion due to fibre sizing, surface treatment, matrix modulus etc to be easily identified, but there is some ambiguity as to how these observations relate to the situation in a real composite. To overcome this restriction a recent approach is to perform fragmentation tests on multi-fibre composite specimens consisting of a monolayer of two or more equispaced fibres in epoxy [1]. This enables the interactions between fibre breaks in neighbouring fibres to be observed and it allows the effect this has on the stress transfer efficiency of the interface to be determined. Much of the work in this area has concentrated on measuring or modelling the increased stress concentration in a fibre as a result of a break in an adjacent fibre.

Most commercially available carbon fibres are now received with a size coating on the fibre surface. The application of size to a fibre results in an improvement in the stress transfer efficiency of the interface and also alters the failure mode at a fibre break from interfacial debonding to the growth of a matrix crack perpendicular to the fibre. In this study, carbon-fibre/epoxy multi-fibre specimens were prepared in a similar manner to Li *et al* [2] with glass fibres as spacers in the fibre alignment process. Results presented here are confined to specimens with an inter-fibre separation of less than one fibre diameter. This study examines the effect these matrix cracks have on the behaviour of the fibre break progression in multi-fibre composites. Both the length of fragments and the failure mechanisms were monitored continuously throughout the tests.

In all samples a high correlation was observed between breaks in closely spaced fibres. In both sized and unsized fibres the presence of a neighbouring fibre resulted in an increase in fragment length compared to that measured in a single fibre test. Additionally photographic examination reveals that when a break in an adjacent fibre occurs within the stress concentration region of a break in the first fibre the two behave as a single break.

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ON THE MECHANISM OF THERMOPLASTIC MATRIX/SINGLE GLASS FIBRE MICROCOMPOSITE FAILURE

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The single filament composite (SFC) test has been used to investigate the adhesion of thermoplastic polymers (HDPE, polycarbonate, polysulphone, PEEK) to glass fibres. For some of these polymers, the values of the interfacial shear strength (IFSS) have been obtained that exceeded considerably not only the shear strength of the matrix but its tensile strength. The only possible explanation for this (valid for the IFSS calculation both according to Kelly-Tyson formula and within Cox's approach) is an increase in the fibre effective diameter. At the same time, the microscopic inspection of the failure zones evidenced that the samples always failed adhesively. Thus, the thermoplastic matrix/single glass fibre composite failure goes probably in two stages: 1) shear yielding of the matrix at some distance from the fibre surface, accompanied by the fragmentation of the fibre with the 'coating', and 2) debonding of fibre fragments with further stretching. The first stage is a consequence of formation of a polymer sublayer around the fibre, having the structure different from that of the matrix in the bulk (due to transcrystallinity and/or specific interaction between the polymer and the fibre surface). However, the fibre-matrix interface remains the 'weak point' of the fragments; it fails through debonding when the applied load increases at the second stage.

The model of fibre fragmentation process in the SFC test taking the sublayer into account is proposed. The cases of elastic and plastic sublayers are considered separately. The numerical Monte Carlo simulation, proceeding from the mechanical properties of the fibre and the matrix, the assumed characteristics of the sublayer (thickness, tensile modulus, yield strength), and the bond strengths at fibre/sublayer and sublayer/matrix interfaces, gives the fibre fragment lengths distribution at any stress level in the specimen. Comparing this distribution with experimental fragment lengths, we can determine the behaviour of the sublayer (elastic, plastic) for various matrices and estimate its parameters. The possibility of the real (local) adhesional bond strength estimation at both interfaces from the continuously monitored SFC test is discussed for two cases: 1) the specimen failure through the sublayer (coating) present at the fibre surface, and 2) the cohesional failure through the matrix.

THE LOCAL BOND STRENGTH AND ITS DETERMINATION BY THE FRAGMENTATION AND PULL-OUT TESTS

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The mechanical properties of fibre-reinforced plastics are governed, to a great extent, by the matrix adhesion to the fibre surface, i.e. the interfacial bond strength (τ). At recent times, many micromechanical tests intended for the adhesional strength measurement are widely used. However, the results obtained by different techniques (e.g. pull-out and fragmentation tests) are often hardly comparable with each other, because they can differ by several times for the same matrix/fibre pair. At the same time, the bond strength, being a constant for a given composite, is fully determined by the components natures and the conditions of the composite formation, and should not depend on the measurement procedure.

In this paper, a technique of pull-out and fragmentation data comparison is proposed. The concept of the "real" (local) adhesional bond strength τ_{loc} as a characteristic of the interface is discussed. It is demonstrated that, under the routine treatment of the data from the pull-out and fragmentation tests, the adhesional strength τ is explicitly or implicitly identified with the mean interfacial shear stress along the fibre at the end of the specimen testing, rather than with the proper τ_{loc} parameter. Since the interfacial shear stress depends not only on the matrix, fibre and interface properties but, to a considerable degree, on the loading conditions, different techniques cannot help giving different τ values. However, experimental plots of the debonding force vs the embedded length (the pull-out test) and the mean fibre fragment length vs the specimen elongation (the continuously monitored fragmentation test) contain all necessary information to calculate τ_{loc} . The τ_{loc} values for adhesional joints between glass fibres and elastic polymer matrices (polycarbonate, polysulphone, polyetheretherketone), calculated from our experimental pull-out and fragmentation data according to a model similar to those by Cox and Greszczuk, appeared to be practically independent of the testing technique. For matrices exhibiting plastic behaviour under stretching (fluoroplastics, polypropylene) a more sophisticated model is proposed taking into account the finite length λ of the region at the interface where matrix yielding actually occurs.

The Monte Carlo computer simulation of the fragmentation test resulted in different fragment lengths distribution functions for different models at any specimen elongation from the beginning of the fibre debonding or matrix yielding. The possibility of exact τ_{loc} and λ calculation proceeding from these functions is discussed as well as some other problems of pull-out and fragmentation data interpretation.

ASSESSMENT OF INFLUENCE OF INTERFACIAL PROPERTIES ON STRESS TRANSMISSIBILITY IN COMPOSITE BY NUMERICAL APPROACH

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Abstract

In a single filament embedded tensile test, the fiber fragmentation behavior has mainly been studied using the Kelly-Tyson model, which is obtained from the critical fiber length. We investigated the stress transmissibility on interface in composites under various interfacial mechanical property by using initial stress of fiber fragmentation and single filament tensile strength.

In this paper, we propose a numerical model which can evaluate the influence of interfacial properties on the stress transmissibility of interface. In this numerical model, fiber, matrix and interphase are modeled for two dimensional finite element analysis independently. The aim of this modeling is that express a stress distribution in each region in the case of single filament embedded test. We calculated the stresses transfer from matrix to fiber by passing interphase by linear analysis. In this calculation, the material properties systems of interphase were set to be two types such as isotropic or orthotropic to estimate the material properties of interphase by numerical analysis and experimental results.

Regarding the analytical results, it is guessed that it is difficult for isotropic interphase to express the stress transfer of actual interphase, because the interphase tensile modulus increases in proportion to an increase of interphase shearing modulus. However for orthotropic interphase, it is realized that it is realistic to express actual interphase bearing stress transfer from matrix to fiber, because it can examine an influence of interphase shearing modulus independent of interphase tensile modulus.

Therefore it was obvious that the numerical approach by using this proposed model will be more desirable to examine an influence of interfacial properties on Stress Transmissibility.

Moreover we can get another result from axial stress distribution. The fiber fracture mode is drastically changed interphase shearing modulus. So in high shearing modulus in interface as compare with that in matrix, the stress concentrated area arise near the first rupture point of fiber. From these result, we can consider that the mechanism of fracture of fiber in composite is affected by material properties system of matrix and interphase and proposed model is useful to evaluate these stress transmissibility on interphase.

IMPACT DAMAGE AND RESISTANCE OF QUASI-ISOTROPIC WET AND DRY T300/914C LAMINATES

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Moisture absorption in carbon/epoxy composites has been shown to affect the failure modes involving fracture in the region of fibre-matrix interface. The moisture absorption in T300/914C composites has been shown to cause plasticization of the matrix as manifest by changes in fracture characteristics, and changes in the glass transition temperature (T_g) as measured by Dynamic Mechanical Thermal Analysis (DMTA). Double Cantilever Beam (DCB) and End-Notched Flexural (ENF) tests were performed respectively to measure Mode I and Mode II fracture toughness and to determine the characteristics of the various fracture surfaces for both wet and dry specimens. The wet specimens, prior to testing, had been immersed in water at 70°C for about seven weeks whilst the dry specimens had been dried at 80°C until equilibrium weight was attained. This paper describes the findings of an investigation of the failure of wet and dry T300/914C quasi-isotropic laminates as a result of low velocity impacts. The impact resistance, as measured by the extent of the projected damage area, was found to increase with moisture absorption. The fracture surfaces at the various layers of the laminate have been examined using optical and scanning electron microscopy. It was found that the features of the delaminated surfaces varied depending on its depth in relation to the laminate stack. The failure mode at each delamination surface was categorised based on a comparison of its characteristics with those of the Mode I and Mode II fracture surfaces. The relationship between impact-induced damage of the wet and dry specimens and Mode I and Mode II fracture toughness was then discussed with reference to this categorisation.

SURFACE DAMAGE CHARACTERIZATION OF CARBON CARBON COMPOSITE MATERIALS IN BRAKING APPLICATION

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This paper deals with composite materials whose surface is damaged by braking applications.

Composites have unique advantages over monolithic materials, such as high strength, high stiffness, long fatigue life, low density, and adaptability to the intended function of the structure. A number of graphite-fiber-reinforced materials have been developed for improved surface properties in friction and wear behavior. We studied different carbon fiber reinforced carbon composite materials (C/C) which have been used in a wide variety of tribological applications such as brake discs. Such materials are used owing to their ability to convert a large amount of kinetic energy to thermal energy in a short time. Although the wear and friction of non metallic solids have some fundamental similarities to those of metals, there are also significant differences in the wear mechanism involved as well as the level of friction in wear.

The mechanical behavior in the wear phenomenon of surface composite materials remains to be understood. In the local approaches -level of constituent-, composites are damaged by matrix and fiber cracking, invisible micro-failure, and mostly interfacial phenomena as delaminating, debonding...

In this study, by using a macroscopic approach we attempted to determine the damaged thickness of the C/C materials after braking. A simple mechanical model was developed in order to localize the thickness of damaged surface after braking.

A specific compressive test is presented here : samples extracted by machining from damaged brake discs are submitted to compressive loading. As damaged zone does not bear the same elastic characteristics, as those of non-damaged part, the elastic center of the sample does not coincide with its geometrical center. Consequently, this shift induces a rotation of the sample head with the help of a special device. As such, it is possible to subtract the additional bending caused by the experimental defects while keeping the rotation which is related only to the damaged zone. Of course, this device must be further improved, nevertheless, it already allows to detect fine damaged zone localized near the surface of the composite materials.

To sum up, our approach, which has been corroborated by micro-observations, allows to gain further insights of surface damaging phenomena.

PHENOMENOLOGICAL ANALYSIS OF MICROPHASE SEPARATION
REGION IN RELATION WITH SAXS INVESTIGATIONS
OF POLYMER BLEND FIBRES.

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In this paper the obtained results of investigations of supermolecular structure and microstructure of multiphase polymer systems are presented. The two compounds fibres were formed from different semicrystalline and amorphous polymers. The supermolecular structure was characterized by degree of crystallinity, the value of the long period and the thickness of the transition layer between phases. The values for the thickness of the diffuse phase boundary were evaluated by means of Ruland's method. The crystalline lamellae are separated (center- to - center) by the long period. The average values of the long period were determined both from the one dimensional scattering function and from one dimensional correlation function. In order to determine the aggregation of the dispersed phase, the analysis of microstructure was performed based on Takayanaga's model. During the formation process of blend fibres with content above 10% of the dispersed phase, values of geometrical parameters assure the balance between surface separation energy of homogenous phase and energy of molecular cohesion of aggregation process. Based on the phenomenological analysis, the macroscopic condition of such balance was given. Values of model and empirical strength and breaking stress, were taken as a criteria of adequacy of model parameters with microstructure of fibres. It makes possible to predict strength properties of blend fibres by computer simulation.

CHARACTERIZATION OF INTERFACES IN COMPOSITE MATERIALS BY OPTICAL FIBER SENSING

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Abstract

The aim of the reported work was to investigate the potential of embedded optical fiber, (OF), to serve as micro-sensor for the characterization of interfacial shear strength, (IS), and residual thermal stress fields in composite material.

This task was addressed by analyzing the modulation of transmitted light in OF embedded in a composite material, along the lines of the so called 'smart materials' approach.

The basic idea behind our approach is that: if the stress level at the interface, introduced by thermal loading, exceeds the IS, interfacial failure will occur thus modulating the transmitted light in an irreversible fashion. If no interfacial failure takes place, then the thermal cycle will result in a reversible light modulation.

Tests were conducted on OF with an aluminum jacket, on which a copper layer was deposited to simulate a matrix. This model composite material was thermally cycled while light was transmitted through its core. It was found that light intensity was modulated along with the temperature changes and the number of thermal cycle. The modulated light characteristics in the first cycle are different than in later cycles. It is possible that the resulting stresses in the first cycle were higher than the IS, and caused interface failure resulting an irreversible change in the transmitted light. Conversely, during the following cycles the modulation was reversible. This may indicate that events which took place during the first cycle, do not occur later. In addition, OF without any coating were thermally cycled in the same manner as the coated fibers. In this case the light transmission response was the same for all the cycles.

In order to better understand these indications, another experiment was conducted, i.e., the electrical resistance between the copper coating and the aluminum jacket was measured during thermal cycling. It was found that the electrical resistance in coated fibers was different in the first cycle than that measured for the rest of the cycles. However, for the fibers without coating the electrical resistance was the same for the first and the rest of the cycles.

ORIGIN, MORPHOLOGY AND CRYSTALLOGRAPHY OF TRANSCRYSTALLINITY IN POLYETHYLENE-BASED SINGLE POLYMER COMPOSITES

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Under certain conditions a transcrystalline layer can form on the fibre surface in fiber-reinforced thermoplastic matrix composites. The presence of a transcrystalline interlayer has been reported in some cases to improve the mechanical properties of composite materials by relieving the residual thermal stresses which may arise from the differential shrinkage on cooling of the matrix and reinforcement.

This work focused on the characterization of the various kinds of transcrystallinity obtained in a polyethylene-based single polymer composite, emphasizing its origin, morphology and crystallography, in relation to the processing conditions of the composite material. The crystalline morphology of the HDPE matrix varied significantly with the crystallization temperature. Accordingly, when the melt was rapidly ice-water quenched (IWQ), relatively large spherulites resulted, which grew until colliding with each other. When the melt was slowly air quenched (AQ) at room temperature, a banded spherulite morphology appeared, comprising more ordered spherulites. Under isothermal crystallization conditions, above 125°C, a non-spherulitic, rodlike crystalline morphology was observed.

The morphologies of the transcrystalline layers obtained under the different processing conditions were found to be similar to the crystalline morphology which developed in the bulk matrix, under the same conditions. Accordingly, smooth and banded transcrystalline morphologies developed under IWQ and AQ conditions, respectively, and a third kind of transcrystalline morphology based on epitaxial growth of a single layer of rodlike crystals on the fiber surface was developed under isothermal conditions.

X-ray diffraction patterns of the transcrystalline layer showed a highly ordered structure, with the a -axis of the crystallites inclined at an angle of 39° to the fiber axis, while a totally random crystal orientation was observed in the surrounding bulk matrix.

ASSESSING THE EFFECTS OF FIBRE SIZING, MATERIAL PROCESSING AND TEMPERATURE UPON THE STRESS-TRANSFER CHARACTERISTICS IN MODEL COMPOSITES

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The micromechanics of reinforcement of a model composite system consisting of continuous high-modulus (HM) embedded in an epoxy resin have been investigated as a function of (a) fibre sizing (b) processing conditions and (b) elevated temperature. The composite was subjected to incremental tensile loading up to full fibre fragmentation, while the stress in the fibre was monitored at each level of load using the new technique of Remote Laser Raman Microscopy (ReRam). To our knowledge this the first time that the stress transfer characteristics are determined at elevated temperatures with this technique.

The average stress in the fibre increased linearly with applied matrix strain up to first fracture. After fracture, the stress in the fibre was found to build from the tips of the fibre breaks, reaching a maximum value in the middle of each fragment. A compressive stress was developed at the location of the fibre breaks resulting from the energy released on fracture and the subsequent fibre recoiling. The shape of the load transfer profiles at moderate levels of applied composite strain, indicated that the fibre sizing had very little effect upon the stress transfer efficiency at room temperature. However, at very high strains considerable differences in the stress transfer profiles and the developed damage zones could be observed. The maximum interfacial shear stress developed in the sized and unsized systems was of the order of 40 MPa. The extent of the interfacial damage zone increased almost linearly with applied strain. Elevated temperatures- below the matrix T_g - affected considerably the stress transfer characteristics of both sized and unsized fiber systems. This led to a significant increase in the transfer length and the interfacial damage zone and to a reduction in the maximum interfacial shear stress developed in each system. These results will be compared with existing analytical models and useful conclusions will be drawn.

THE CHANGE OF THE MORPHOLOGY OF THE FIBRES ON THE BASIS
OF POLY(ETHYLENE TEREPHTHALATE) - FIBROIN MIXTURES IN THE
STRETCHING PROCESS ABOVE THE GLASS TEMPERATURE OF MATRIX POLYMER

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The possibility of formation of poly(ethylene terephthalate) (PET) - fibroin (FN) molecular mixtures with FN content of up to 10% (by weight), in the forms of concentrated solutions or in solid state, was demonstrated earlier. Model fibres, characterized by amorphous low-oriented structure, were spun from PET-FN mixtures by wet spinning process. The increase of FN content in the mixture to 10...12% (by weight) resulted in a certain increase of fibre tenacity, i.e., from 7.2 to 9.8 cN/tex at 8...10% elongation. The glass temperature of PET fibre free from FN additions, is 70°C. The addition of 5% FN (by weight) to the fibre matrix resulted in a rise of T_g to 78°C and addition of 10% FN (by weight) resulted in $T_g=86^{\circ}\text{C}$.

The structural changes of PET fibres, containing 10%, 20% and 30% FN (by weight) were investigated in the process of orienting stretching at the rate of 1...5 m/min⁻¹ at 100°C, 120°C and 130°C in the direct stream medium.

Birefringence, Δn and density, ρ , in n-heptane at 25°C of drawn fibres were determined. The fibre morphology changes after its stretching were inspected using optical and scanning electronic microscopes. If isothermal draw ratio is increased by 5 times, the relative tenacity of the fibre containing 10% FN (by weight) goes up to 46...49 cN/tex at 12...14% elongation, while PET fibre draw ratio under the same conditions was only 32...34 cN/tex with the same elongation.

Observation using an electronic microscope, of oriented fibres spun from polymer mixtures, revealed in matrix PET a formation of fibrous structures of 0.6...1.3 micrometer in diameter and 10..14 micrometer by length. The residue left after dissolving the modified fibres in hexafluoro-isopropanol, was identified as FN. Spontaneous aggregation of FN into fibrillar structures is intensified when stretching temperature and draw ratio are increased.

Interfacial adhesion in the presence of water

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The effect of water penetration on the initiation and propagation of an interfacial crack in model quartz/epoxy microcomposites is studied. An Arrhenius model is used to describe the kinetics of debonding initiation. Energy-balance approaches are used to provide a quantitative interpretation of the initiation and growth data. The effects of temperature and immersion time in distilled water are discussed.

Microphenomena in advanced composites: Review of energy-based interpretations of interfacial adhesion

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In recent years, the quality of the fiber-matrix bonding in composites has been quantified by means of a single mechanical parameter, the interfacial shear strength, based on measurements made using micromechanical techniques. However, it has gradually appeared that this parameter is both ambiguous in terms of its physical meaning and, at the same time, difficult to measure reliably in many cases. Moreover, different micromechanical techniques yield differing values of the interfacial shear strength. Finally, it has been suggested in a few studies that it may not be the critical factor governing fiber-matrix debonding. Here an energy-balance approach is proposed, by which the degree of fiber-matrix bonding is now quantified by a new measurable parameter, the interfacial energy. This latter is a function of the fiber geometrical and mechanical characteristics, the stress transfer length, and the debonding length. The validity of the approach is discussed in the case of the single-fiber composite test, in which progressive fragmentation of a single brittle fiber in a more ductile polymeric matrix takes place, using data for E-glass, quartz, and silicon carbide fibers embedded in a uv-curable urethane-acrylate resin.

Transcristalline interphases: Microindentation and AFM results

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Recent results regarding the measurement of isotropic and anisotropic microhardness of transcristalline microstructures are presented. The data were generated by means of two techniques, namely, a microhardness tester using Vickers and Knoop modes, and atomic force microscopy (AFM) in the contact and non-contact modes. The materials used were HM carbon fibers in either isotactic polypropylene or polycaprolactone matrices. The possibility of using such techniques as a measurement of the anisotropic Young's modulus of transcristalline polymers is discussed.

**Study of the Effect of Transcrysallinity in Kevlar®149-Poly(caprolactone)
Composites by Means of the Microbond Test**

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The effect of transcrysallinity on the interfacial mechanical properties for thermoplastic polymer composite was investigated by the means of the microbond or droplet pull-out test. Kevlar®149 fibres proved to be a good site for the nucleation and transcrysalline growth of poly (caprolactone) (PCL) polymer, hence allowing for almost fully transcrysalline droplets to be made. Fully amorphous microbond samples were made by quenching the molten droplet with a cold stream of nitrogen gas. First glance at the results indicate that the presence of transcrysallinity has no effect on the strength of the interface. However, when analysed with the 'simple' *average* shear stress method the interfacial shear strength results obtained indicate a very slight weakening of the interface in the presence of transcrysallinity. Cross section of the droplets, with the fibre in the middle, were obtained by polishing and microtoming, and subsequently observed in the optical and scanning electron microscopes, respectively.

STRUCTURAL INHOMOGENEITIES OF LIQUID EPOXY RESIN.

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Epoxy resins (ER) have become the most common matrix for composite materials, therefore, these resins has been a subject of considerable practical and scientific interest to many investigators. But majority studies have been made on the properties and structure of ER during and after curing. This study involves an Electron Microscopy (EM) investigation, DSC, positron annihilation spectroscopy (PAS) of liquid ER of the diglicidil ether of bisphenol (ED-20, ED-16). Using the freeze-fracture method EM revealed the presence of nodules on the order 300-400 \AA in diameter in liquid ER. Size and density of packing of nodules one can change, for example, by ultra-sound treatment. Endothermic peak was observed at 79°C with enthalpy value 4,87 kJ/mol in the base line of Percin-Elmer DSC 7. Positron lifetimes were measured as a function of temperature. Results of PAS showed, that the free volume of ER has two temperature intervals of thermal expansion and transition temperature was found about 69°C . The mean hole size increases from 2,4 to 3,9 \AA from 20 up to 60°C , while its concentration decreases. Above 60°C the mean holes size is constant, but its concentration increases. All experimental results are accounted by existence of molecular aggregates or structural inhomogeneity of liquid ER. According to numerous studies about the presence of nodular morphology in curing ER, one can confirm, that the correlation exists between the morphology of liquid oligomers and their network solid polymers.

SLOW POSITRON SPECTROSCOPY : A NON-DESTRUCTIVE ALTERNATIVE TO PEELING TESTS FOR ADHESION ASSESSMENT

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The quest for non-destructive assessment of interface microstructure has long been, and remains, a subject of importance in the production of multilayers, particularly for metal coating of polymers. Indeed, although surface pretreatments are designed to improve metal adhesion, final certification of the processes relies on peeling tests which are irreversible and difficult to reproduce. In an attempt to demonstrate that these problems can be overcome by using positron implantation spectroscopy, we investigated aluminium coated polypropylene (PP) and high density polyethylene (HDPE) which not only represent simple bi-layer models but are actually used in a wide range of industrial applications.

Using the UEA-Norwich ²²Na isotope based beam facility which is capable of probing polymer depths ranging from a few nanometres up to about 20 μm depending on the incoming positron energy, we studied HDPE and PP films at each main step of the coating process: i.e, as received, He or CF_4 plasma pretreated, and after Al coating.

Correlating the positron depth profiles with peeling test results for various coating conditions, we tentatively identify features in the energy dependence of the photopeak lineshape parameter which might indicate the quality of the interface.

THE ROLE OF INTERFACIAL TENSION IN PRODUCTION OF ASPHALT PAVINGS AND CEMENT CONCRETE

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The research here presented was made in order to find the regularity of a phenomena observed in asphalt mix produced when experimenting with different methods of mixing. The appearance of the phenomena was irregular, showing an unpredicted increase in glossiness and creaminess of mix, previously only experienced at increase in the bituminous liquid content of the mix.

When the bituminous liquid is mixed with the aggregate, an influence of interfacial tension (IFT) develops in the liquid through adhesion to the surface of the aggregate particles. It was observed that the IFT in the liquid of conventional mix changed with temperature of paving. Thus, two effects of the IFT were observed. 1) the paving deforms at low IFT due to high temperature, and 2) cracks at high IFT due to low temperature. The behaviour of the paved mix, in relation to climate conditions, is irregular.

A third effect of the influence of IFT appeared when applying new theories for production that lead to dispersion of particles in the bituminous liquid and thus, to mix in state of suspension. It was discovered that the IFT from dispersed particles made the glue phase tough.

To assemble and retain the various fractions of fine and coarse aggregate particles of the asphalt mix in the closed volume of liquid of the suspension, a mixing process leading to a high degree of self-assembling of the aggregate particles and the liquid was required. The motor of the self-assembling system came to be the third effect of the IFT, developed through dispersion, by a special technique of discharge of the materials in to the mixer. Thus omitting the not wanted first and second effects of the IFT. The inertia of toughness in the glue phase reduces the sensitivity of paving to temperature and the behaviour in relation to climate conditions becomes regular.

The self-assembling system for the production of asphalt mix in state of suspension, came also to be used in production of cement concrete. The third effect of IFT from dispersed particles in the water, appeared also in the glue phase of the hardened cement concrete. This was confirmed by dispersion tests on glue phase of the hardened concrete; brittle in the conventional concrete and tough in the concrete of the research. The inertia of toughness delays the ageing of the glue phase and the destruction of the concrete.

Effects of fiber coatings on static and impact mechanical properties of glass-reinforced composites.

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Glass fibers were coated with an elastomeric material based on an epoxy-amine formulation. The process involved the continuous impregnation of fibers with a solution of the monomers, followed by solvent evaporation and cure along heated tubes. Temperature profiles were selected to attain a high conversion level at the exit of the impregnating device while avoiding monomer losses. The coating thickness was regulated by the concentration of the impregnating solution.

Unidirectional composites including the coated fibers in a commercial epoxy-anhydride matrix, were produced using combined techniques of filament winding, vacuum bag, and autoclave processing. The porosity of the different composites was evaluated using conventional density techniques as well as digitalized-image processing.

The effect of the elastomeric coating on mechanical properties measured at low velocities (longitudinal and transversal flexion, SBS), was either negligible or slightly deleterious. However, the statistical dispersion of experimental results was reduced.

But in a high-velocity mechanical test (transversal impact), a significant improvement was observed when using coated fibers. Observation of fracture surfaces by scanning electron microscopy revealed a higher fiber matrix adhesion derived from the use of the elastomeric coating. This constitutes a possible explanation of the observed increase in the impact resistance.

A general discussion of the effects produced by coating the fibers with an elastomer is provided.

THE RÔLE OF THE INTERFACE IN THE COMPRESSIVE BEHAVIOUR OF INTERPLY HYBRID COMPOSITES.

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Interply hybrid composites, where laminates containing different fibres are stacked in a symmetrical pattern, are of interest to engineers because of the possibility of achieving a desirable balance of mechanical properties in a cost effective manner. Such composites can be subject to compressive forces either as a result of direct loading or flexure. In such situations the compressive and shear modulus of the matrix play an important role in terms of supporting the fibres to prevent buckling. However, the interfacial adhesion is also important as it not only controls stress transfer but also the shear modulus of the composite and hence the microbuckling stress.

In this paper results obtained for the compressive behaviour of interply hybrids consisting of either polyphenylene sulphide thermoplastic resin or epoxy thermosetting resin, reinforced with various symmetrical configurations of E-glass and carbon fibres are presented and compared. Interlaminar shear and transverse tensile test results together with post-failure microscopic examination are used to explain the rôle of the interface in the compressive behaviour recorded.

For unidirectional interply hybrid composites the rule of mixtures was found to be an acceptable model to predict the secant modulus of hybrids with both thermosetting and thermoplastic matrices. The same model also gave an acceptable prediction of the failure stress for thermoset matrix composites but was not successful in predicting this property for thermoplastic matrix composites. The failure stress for these materials was found to be dependent on the relative carbon volume fraction and the stacking sequence, with relatively higher values being recorded for hybrids where carbon laminates were sandwiched between glass laminates.

An enhanced failure stress was observed in crossply hybrid composites when the outer laminates consisted of either longitudinal glass fibres or transverse carbon fibres. This behaviour could be partly explained by interlaminar shear testing and microscopic examination which revealed that the interface adhesion between the carbon and the matrix was much greater than for the glass, for both types of matrix, which led to relatively poor transverse properties in glass fibre reinforced laminates. In unidirectional composites both types of laminate failed under compressive loading by kink band formation but the glass laminates also exhibited considerable longitudinal splitting. In crossply composites the transverse laminates failed by shear and often delamination occurred at interfaces where the fibre orientation angle changed.

PREDICTION OF INTERFACIAL STRENGTH DISTRIBUTION USING A SINGLE-FIBER COMPOSITE TEST

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Traditional application of experimental methods of interfacial strength evaluation, including a single-fiber composite test (SFC), shows extremely high variability of the results. It is our premise that this unsatisfactory variability may be explained by actual random nature of fiber and interfacial strengths, as well as interfacial debonding process. Therefore, the purpose of the research is to offer an approach of evaluation of interfacial strength distribution, which will be able to take into consideration actual strength (toughness) variability of SFC components, in a very simple form. The approach presented is based on our recent results of SFC statistical simulation and a respective probabilistic model. Statistical information regarding the fragment length distribution, along with the fiber strength distribution (FSD) and the interfacial debonding length (IDL), are necessary experimental data. Here, statistical parameters of both FSD and IDL are obtained using a SFC test. Thus, a reliable technique of FSD evaluation "in-situ" is offered as well. This "in-situ" technique seems to be much more convenient than traditional test of monofilament gauge. Experimental confirmation of the approach is considered on the examples of glass/epoxy SFC with different fiber surface treatments. A significant difference between traditional and proposed approaches is shown. The approach is presented as series of dimensionless nomograms, which reflect a simple character of its application.

MICROWAVE PROPERTIES IN THE X-BAND AND SOME TENSILE PROPERTIES OF CARBON FIBRE-POLYPROPYLENE AND CARBON BLACK- POLYPROPYLENE COMPOSITES

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ABSTRACT

Insertion loss, return loss and electromagnetic shielding effectiveness of carbon black and carbon fibre filled polypropylene composites were studied in the 8 to 12 GHz frequency range. Both electromagnetic and mechanical measurements were performed at filler concentrations of 15, 25, 35 and 40 wt%. Composites containing carbon fibres showed better shielding effectiveness than carbon black filled composites. This was attributed to the formation of better filler interconnections within the matrix. The maximum shielding values obtained for carbon fibre filled composites was over 40 dB for 35 wt% concentration. Conductivity of composites increased with the filler concentration and the critical concentration for carbon black and carbon fibre filled composites were observed around 25 wt% and 15 wt% respectively. Stress strain behaviour at various compositions and variations of the Young's modulus, ultimate strength and elongation at break with respect to filler concentration were also determined. Stiffness and brittleness of the composites increased with the increase in the filler concentration. The ultimate strength of carbon black filled composites increased with the filler content whereas the ultimate strength of carbon fiber filler composites remained constant at a value smaller than that of pure polypropylene. Elongation at break values for all composites dropped sharply with the filler content. "

EFFECT OF INTERFACE ON DEGRADATION OF GLASS FIBER/VINYLESTER COMPOSITES

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Composites are attractive for use as structural materials under various environmental conditions as a result of their high strength-to-weight and stiffness-to-weight ratios, and a high level of fatigue resistance and good chemical resistance. However, the degradation of the fiber/matrix interface can have a profound influence on the resistance to environmental attack. The present study deals with composites formed from with E-glass fibers and vinylester resins which are under consideration for use in infrastructure applications.

Samples of net resin and composites were tested using dynamic mechanical thermal analyses (DMTA) and differential scanning calorimetry (DSC) after exposure to a number of environments that included standard buffer solutions of pH 4, pH 7 and pH 10, distilled water at room at elevated temperature and a cycling type experiment. During the testing period changes of the viscoelastic moduli in the glassy and rubbery states, glass transitions, heats, and weights were monitored. It was determined that the parameters obtained directly from DSC and DMTA experiments had no considerable change over the period of exposure (6 months) to the selected environments. Small changes of T_g after about two weeks exposure were attributed to a competition of physical and chemical aging mechanisms.

Multifrequency DMTA experiments have been carried out to calculate the activation energies of the sample glass transitions. It was found that the energies of activation for composite samples decreased with the increase of exposure time. Thus, a sensitive parameter to detect environmental influence on composite properties has been suggested. The interface contribution was elucidated through the comparison of response from the neat resin samples and the composites.

Session 5

ADHESION - MOLECULES AND MECHANICS

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This paper describes new ideas about adhesion. In particular it emphasises the difference between adhesion at the molecular level and adhesion in engineering terms. There is no doubt that molecules of solid materials are attracted to each other by van der Waals and other influences. Also, they can be separated by applying mechanical forces. The problem is explaining the connection between molecular attractions and mechanical adhesion measurements. False ideas such as 'keying' and 'glueing' require critical assessment because they confuse molecules and mechanics. Interesting mechanisms such as 'adhesive hysteresis', 'adhesive stringing', and 'adhesive clustering' deserve evaluation. A rational theory of these and other interface phenomena should be based on the theoretical concept of reversible work of adhesion. However, it is necessary to distinguish this thermodynamic work of adhesion from the measured quantity of adhesive energy, which includes the extra energy required to restructure the interface as surfaces move.

Abstract for ICCI - VI

Fundamental studies of interfacial shear between solid surfaces

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The shear properties of different solid-solid interfaces play an important role in the properties of advanced composite materials. Using a surface force balance to measure simultaneously normal and shear forces between sliding solid surfaces, we have investigated interfacial shear in a number of model cases. The shear of both polymeric and monomeric interfacial species has been studied with unique sensitivity and resolution. In particular, we have probed the nature of yield stress on shear and of stick-slip behaviour on sliding, when the interfacial shear zone is only a few molecular monolayers thick. We find both liquid-solid and solid-solid transitions as the thickness of the interfacial layer decreases, and have probed the effect of shear rate on the critical yield stress.

Session 6A

The effect of absorbed moisture on damage development in polymeric composites

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The effect of absorbed moisture on the long-term durability of polymeric composite materials has been studied. In particular, the effect of moisture on the interfacial strength, the ply stress at which debonding begins, and the ply stress at which transverse cracking occurs in unaged composites and composites aged to saturation in simulated seawater have been investigated. DGEBA epoxy reinforced with E-glass and with carbon fibers have been considered.

Microindentation tests in E-glass/epoxy composites have indicated a reduction of 25% in the interfacial strength for shear loading due to absorbed seawater, while direct observations in an environmental SEM of debonding and transverse cracking in E-glass/epoxy composites loaded in the ESEM have indicated a reduction in the required stress of less than 15% due to absorbed seawater. These differences are explained the differences in the effect of the absorbed seawater on the residual stress for the two different loading conditions (shear versus normal loading). Less than 15% reduction in both the interfacial strength (measured using single fiber fragmentation testing) and the stress required to give transverse cracking (measured using an ESEM with a loading stage) have been observed in due to absorbed seawater in carbon fiber/epoxy matrix composites.

The effect of the microstructure, including resin rich regions and voids, on damage initiation and propagation have been observed and found to be very significant. For example, residual stresses around a resin rich region will be tensile whereas residual stresses at a fiber matrix interface will be compressive. Moisture effects can be quite different in the presence of such heterogeneities.

Finite element analysis has been used to evaluate the residual stresses and the local stresses at the fiber matrix interface in these studies.

HETEROGENEOUS PHASE SEPARATION AROUND FIBRES IN EPOXY/PEI BLENDS AND ITS EFFECT ON COMPOSITE DELAMINATION RESISTANCE

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Blends of DGEBA-type epoxy with poly(ether imide) thermoplastic modifier (PEI) were prepared and combined with unidirectional glass fibre tape to produce pre-pregs. These pre-pregs were laid-up and cured into unidirectional fibre-reinforced composites. Delamination coupons were tested under mode I, mode II and under mixed-mode I/II loadings, using the latest NASA mixed-mode bending rig.

The phase separation in the curing epoxy/PEI blends was studied extensively using hot stage microscopy and was compared to that developing in the presence of individual glass, carbon and aramid fibres. The effect of cure temperature, PEI content, PEI functionality, PEI molecular weight, epoxy resin molecular weight, hardener type, fibre volume fraction and fibre surface treatment were investigated. In the presence of glass fibres, the phase separation in epoxy/PEI blends proceeded depending on the PEI content. In contrast, it was totally unaffected by the presence of carbon and aramid fibres. The most striking feature was the development of a discrete layer around glass fibres for PEI concentrations between 15 and 20 wt %. It was shown by optical, scanning and transmission electron microscopy that the layer developing around glass fibres is thermoset-rich, whatever the PEI concentration. This was attributed to preferential wetting of glass fibres by the epoxy resin rather than by the PEI phase. The extent of the thermoset-rich phase appeared dependent upon the exact processing conditions and on the proximity of other fibres (i.e. volume fraction of fibres in the composite).

This heterogeneous phase separation was shown to have little effect on mode I delamination resistance of glass fibre-reinforced composites coupons. However, as mode II loading was introduced, the delamination resistance was lowered significantly by the presence of the thermoset-rich phase surrounding glass fibres. It was shown that the thickness of the interphase affected the delamination behaviour of the composite : the thicker the layer, the lower the fracture resistance measured. The potential benefit of thermoplastic modification can be completely lost under these circumstances.

Whilst the observations reported here relate to a specific epoxy/thermoplastic blend and glass fibres, the phenomenon of heterogeneous phase separation is not limited to this system. Most of the newer commercial matrix resins are blends of a similar type as that investigated here and are thus likely to exhibit some level of heterogeneous phase separation under certain circumstances. Any observations of this kind made on commercial composites go largely unreported. Nevertheless, such effects could be the underlying cause of unexpected variations in mechanical properties, especially when the composite is subjected to any significant shear stresses. Study of the reasons for heterogeneous phase separation in thermoset/thermoplastic blends, with the aim of preventing the creation of brittle interphase regions in commercial composites, thus appears deserving of attention.

UPPER-BOUND ANALYSIS OF INTERFACIAL EFFECTS ON TRANSVERSE FAILURE INITIATION IN POLYMER COMPOSITES

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Abstract

Transverse failure is an important mechanism of failure in polymer composites. In pressure vessels and pipes, fluid leakage is a common design criterion. Leakage often occurs through paths provided by transverse cracks linked together. Even for cases when final failure occurs by fiber fractures, transverse cracking is of importance since it is the first major type of damage in the material.

The transverse failure initiation strain is sensitive to matrix and interface properties. The present study considers a material with a perfect interface. This provides the best performance we can expect out of a material if no debonding occurs. For typical polymer composites, the fiber is much stiffer than the matrix. For this reason, a highly triaxial stress state is created in the matrix. This was demonstrated by finite element analysis. Experiments were then carried out with glassy epoxies, demonstrating the low strain to failure of epoxies under composite-like stress states. A failure criterion was suggested based on a critical value for the dilatational energy density. Experimental data for different stress states were in support of this criterion.

Having established a criterion for matrix failure, finite element analysis was carried out in order to investigate transverse failure of glass fiber/epoxy at different fiber contents and fiber packing geometries. Plastic yielding was also considered. For all cases failure initiated in a region very close to the interface. The strain to failure initiation was in general quite low. Interlayers between fiber and matrix were also investigated. Intermediate modulus layers gave negligible effects on global strain to failure initiation. Positive effects were found for thin rubbery interlayers. The maximum radial stress is likely to cause debonding for the investigated case. For this reason the position of maximum radial stress was investigated and compared with the position of maximum dilatational energy density in the matrix. These positions coincided for the large majority of investigated cases. A consequence of this is that is not easy to distinguish between interfacial debonding and matrix failure as initiation mechanisms. It is also apparent that improvement of interfacial debonding resistance does not necessarily lead to a high strain at transverse failure initiation.

MICROMECHANICAL ASPECTS OF CRACK BRIDGING IN ARAMID/EPOXY COMPOSITES

by

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Raman spectroscopy has been used to study the effect of matrix cracking on the deformation micromechanics of Twaron aramid fibres embedded in a brittle matrix. Compact tension specimens were prepared with fibres embedded in a cold cured epoxy resin normal to the direction of the notch and then pre-cracked such that the crack ran through the fibres. Two types of aramid fibres were used, low modulus Twaron and high modulus Twaron, both in the untreated and surface-activated form. The point-to-point distribution of strain was measured in the aramid fibres both ahead of the crack tip and bridging the faces of a static crack, thus enabling the modes of interfacial failure to be monitored.

Initially, strain profiles were mapped out for an array of fibres behind the crack tip in an unloaded specimen showing that pre-cracking caused debonding and that fibre fracture did not occur. The length of debond was shown to increase with greater distance between the fibre and the crack tip. The extent and direction of debonding was also shown to be dependant on the surface treatment. The specimen was subsequently loaded incrementally and a build up of stress in fibres ahead of the crack tip was measured. Although in most cases the fibre and interface were able to withstand the stress intensification it was sometimes possible to observe interfacial debonding and fibre fracture immediately ahead of the crack tip. The behaviour of fibres bridging the faces of the crack was observed, particularly with respect to the extent of debonding and it was shown that for most cases debonding did not propagate significantly as a result of static loading.

Results were considered with respect to the interfacial properties of each system as determined for single fibre model composites of each system. The findings were then compared to relevant theories of fibre reinforcement and particularly to the Cook and Gordon mechanism [1] of toughening in fibre reinforced composites.

1. Cook, J. and Gordon, J.E., "A mechanism for the control of crack propagation in all brittle systems", *Proc. Roy. Soc. Lond. A* **282** (1964) 508-520.

Session 6B

THEORETICAL CONSIDERATION OF THE SINGLE-FIBRE-PULL-OUT-TEST

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Though in use since several years the significance of the results of the Single-Fibre-Pull-Out-(SFPO)-Test, characterizing fibre-matrix-adhesion, remains controversial. The commonly used data reduction scheme, assuming a constant interface shear stress, is oversimplifying the actual stress distribution essentially. Strong stress gradients at the fibre ends and matrix cannot be correctly described with even highly sophisticated analytical models (let alone shear-lag models). The debonding process is further complicated by thermally induced stresses, fibre-matrix-interface-friction and material inelasticity.

Only numerical analysis can cope with this challenges. The debonding process has been investigated using a finite element model with a fracture mechanics approach. At a first stage, without consideration of friction, thermal stresses and inelasticity, it is demonstrated, that a fracture mechanical debonding criterion (energy release rate) provides a self consistent description of brittle interface crack extension. It becomes obvious, that the SFPO-test induces a pronounced mixed mode interface loading state, that will change dramatically for short crack lengths. Due to independent experimental experience interface failure is mainly controlled by the normal loading component. Therefore a fracture mechanics mixed mode criterion for debonding is used in the model. Mixed mode state and different interface sensitivity towards miscellaneous loading modes turned out to have essential influence on the debonding process.

Debonding crack initiation from the matrix surface will start as stable crack extension even for purely elastic and very brittle systems. After passing a maximum value for the loading force, the crack extension will quickly turn unstable with instant and complete debonding for long free fibre lengths (i.e. compliant loading conditions). Because of the neighbourhood of the matrix surface with its high stress gradients, acting as a disturbance, the stress conditions at the interface crack tip are hardly predictable for short interface crack lengths. They are influenced by arbitrary local variations of the geometry (wetting meniscus), the strongly changing mixed mode conditions and by material inelasticity. Since maximum debonding load appears just in the short crack range, it seems not qualified to characterize adhesion reproducible. In view of the number of rarely known but influential parameters modelling of the correct dependence between maximum debonding force and adhesion seems to be out of reach.

A way out appears by investigating stiff loading conditions with very short free fibre lengths. This configuration allows expansion of stable crack extension beyond the maximum debonding force until crack lengths of nearly 3/4 of embedded fibre lengths, as could be recently confirmed by experimental research. For debonding crack extension along the midst of the embedded fibre length neither matrix surface nor fibre end will have essential influence on the local crack tip conditions. A plateau range occurs, in which energy release rate, mixed mode state and debonding force will show minimal changes and that hence provides more reliable conditions for interface characterization. The model revealed, that the plateau value of the energy release rate (without thermal stresses) may be approximated well by a simple equation for the contribution of the free fibre, in this way offering a chance for easy experimental estimation of interface toughness from the plateau value of the debonding force. Attention of experimentalists should be converted from maximum debonding force to the evaluation of the plateau range.

The incorporation of thermal stresses in a second stage of the analysis reveals their disadvantageous effect on the tests interpretation. Though the plateau range is maintained qualitatively, it is quantitatively shifted by the thermal stresses. Their influence is unnegligible but much more complicated and can probably not be approximated by a simple model. Ahead of the properties of the fibre and the matrix (drop shape, ...) the thermal mismatch between sample holder and matrix drop can be identified as the main source of the (huge) thermal strain energy in the specimen. Because the sample holder is inherent to the SFPO-configuration, a large magnitude of thermal stresses seems to be unavoidable for this test. Therefore it should be asked, if the Single-Fibre-Pull-Out-Test is really adequate or if it should be replaced by a similar test less influenced by thermal stresses. If it could be proved, that the closely related Microdroplet-Pull-Off-Test shows a plateau range too (as may be expected together with less pronounced thermal strains), this test configuration should be preferred for interfacial characterization.

Influence of the thermal history on the results of fragmentation test of high modulus carbon fiber-polycarbonate model composites

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Micromechanical test methods are often used to characterise the fiber/matrix interface in terms of interfacial shear strength. During the preparation of model composite samples, however, residual thermal stresses develop in the matrix, namely along the interface. The build up of these stresses is due to the difference of the thermo-mechanical characteristics of the fiber and the polymer and its extent is significantly dependent on the thermal history of the composite [1].

The aim of this work is to show that, for samples prepared by compression moulding, the cooling rate influences considerably the residual stresses present along the fiber/matrix interface. For that purpose, plaques of polycarbonate containing a high modulus pitch-based carbon fiber were prepared and cooled at different rates. Using polarised light microscopy, a stress pattern along the interface was observed, which was related to the residual stresses developed during the preparation of the composite [2]. They were submitted to fragmentation tests and the results interpreted according to the Fraser-Di Benedetto approach [3]. A considerable dependence of interfacial shear strength on cooling rate was found. Lower cooling rates induce higher interfacial shear strengths. However, they also enhance fiber breakage, due to the difference of the thermal expansion coefficients of the fiber and the polymer. This leads to the necessity of selecting a optimal cooling rate for the preparation of the model composites. Agreement upon this rate, that should depend on the fiber and polymer characteristics, is important for the comparison of results obtained in different laboratories.

1. M. Nardin, E. M. Asloun and J. Schultz, *Polym. Adv. Techn.* **2**, 115 & 161 (1991).
2. M. C. Paiva, M. Nardin, C. A. Bernardo and J. Schultz *Proc. 22nd Biennial Conference on Carbon*, San Diego, USA, 16-22 July 1995.
3. W. A. Fraser, F. H. Ancker and A. T. Di Benedetto, *Proc. 30th Ann. Techn. Conf. SPI/Reinf. Plast. Composite Inst.* (1975), 22-A.

INTERFACIAL CRACK PROPAGATION WITH FRICTION ARISING IN SINGLE FIBER PULL-OUT TESTS

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Commonly, micromechanical tests are evaluated by calculating an 'interfacial shear strength', denying the mixed-mode behaviour of an interface crack. In none of the micromechanical tests, however, a pure mode II failure arises but a mixed mode failure occurs with different mode mixities arising in the respective tests.

As an alternative to the calculation of a failure stress, in this paper, the interfacial fracture process arising in the pull-out test is investigated using a finite element analysis. The analysis reveals that in case of a very stiff testing system, this is, a stiff testing machine and a very short free fiber length, a stable crack propagation can be achieved. The existence of a stable crack is verified conducting pull-out experiments under a microscope. It is shown that the radial stresses are responsible for the crack initiation. However, the mode ratio significantly changes during the crack propagation from prevailing mode I near the matrix surface to prevailing mode II in the remaining part of the interface. Furthermore, the mode ratio strongly depends on the material properties of the two constituents, mainly on the axial youngs moduli.

The results also show that the crack initiation can be determined experimentally from the force-displacement trace as a change of the compliance. This means that the commonly used force maximum is not relevant for the description of the interfacial strength but the force in the moment of crack initiation. The force maximum marks the onset of unstable crack propagation.

In order to overcome the problem of the stress singularity arising at the fiber entry, the energy released during crack extension is used as a material property describing the interfacial toughness instead of a failure stress. For the determination of the energy release rate, a complete simulation of an interfacial crack propagation is performed and the G_I and G_{II} values are calculated. To study the influence of friction, different frictional stresses resulting of different processing conditions are taken into account. The numerical results are correlated to experiments in order to determine the fracture toughness of several material combinations e.g. glass and carbon fibers theoretically as well as experimentally.

Session 7A

ROLE OF INTERFACES IN MODE II FATIGUE DELAMINATION GROWTH OF INTERLAYER TOUGHENED GRAPHITE/EPOXY LAMINATES

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At present the most promising candidate for toughening graphite/epoxy laminates appears to be the concept of 'interlayer'. Interlayer refers to a mixture of thermoplastic particles and thermoset base resin, selectively localized between laminae as a thin resin film. A newly developed interlayer toughened graphite/epoxy has demonstrated excellent compression after impact (CAI) strength and hot-wet characteristics. The toughening mechanism of interlayer has so far been investigated in terms of static mode I and II interlaminar fracture toughness and the improvement in toughness has been shown to be greater in mode II than in mode I.

In this paper the mode II fatigue delamination growth behavior of the interlayer toughened graphite/epoxy laminates were comparatively evaluated together with the other graphite/toughened epoxy laminates and the conventional untoughened graphite /epoxy laminates. Fatigue tests were conducted by using the end-notched flexure (ENF) test specimens, in which the crack length and the mode II energy release rate were calculated from the high accurate measurement of crack shear displacement (CSD).

The results showed that the two kinds of toughened laminates exhibited a relatively higher resistance to the mode II delamination growth at the high delamination growth rate than the conventional laminates. However all the laminates were shown to give almost the same value of the threshold mode II energy release rate, which suggested that the toughened interlayer and the toughened epoxy matrix had no effect for improving the toughness in terms of the threshold mode II energy release rate.

The difference in mode II fatigue delamination growth mechanisms were discussed through the detailed observation of fatigue fracture surfaces by a scanning electron microscope and an optical microscope. Some numerical simulations of crack propagation were conducted based on a two-dimensional finite element modeling. The role of interfaces in mode II fatigue delamination growth were comparatively evaluated based on the observed and simulated results.

MICROMECHANICAL STUDY OF THE INFLUENCE OF INTERFACIAL FAILURE ON THE MACROSCOPIC BEHAVIOUR OF COMPOSITES

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ABSTRACT

The object of this paper consists in developing a micro-macro relationship of Mori and Tanaka's type, based on microstructural parameters (geometrical and mechanical properties of the matrix, the fibers and the interface), in order to predict :

- 1) the tridimensional macroscopic first damage criterion corresponding to the appearance of the first interfacial damage inside composite materials
- 2) the entire stress-strain curves and the loss of stiffness due to the fiber/matrix interface failure.

The behaviour and the damage of such heterogeneous materials are related to the mechanical and geometrical properties of the constituting phases. The matrix, reinforcement and interphase mechanical behaviour laws, the distribution of orientation, aspect ratio, volume fraction of the reinforcement, are the principal factors managing the composite behaviour. In order to relate the microstructure and the local interfacial damage mechanism to the macroscopic damaged behaviour, we establish a micromechanical model based on the micro-macro relationship of Mori and Tanaka.

To take into account the appearance of interfacial cracks, a local failure of damage initiation has been identified by coupling experimental and simulation results. The criterion is then introduced in the model.

The local stresses tensors are calculated in each phase as a function of the applied macroscopic stress and the microstructure parameters. The continuity condition at the interface allows to calculate normal (σ) and shear stresses (τ) all around the fibers. The local damage criterion means that interfacial debonding can occur at a point of the fiber/matrix interface when a combination of σ and τ reaches a level related to the interface strength. For example, in the case of a glass/Epoxy composite, an elliptic local criterion has been identified (see figure 1) :

$$(\sigma/\sigma_0)^2 + (\tau/\tau_0)^2 = 1$$

where σ_0 and τ_0 are respectively the limit normal stress and the limit shear stress on the interface.

The knowledge of this microscopic failure criterion allows to calculate, by using the micro-macro relationship, the combination of tridimensional macroscopic stresses giving rise to the initiation of the first fiber/matrix interface breaking in the composite. For example, figure 2 shows the macroscopic first damage criterion in the case of combinations of tensile and compressive macroscopic stresses. Note that this damage criterion is not symmetrical in tension and compression.

For the second purpose of this paper, damage evolution is introduced in the model at the fiber scale by changing the elastic properties of the fibers. When the failure criterion is activated on a fiber/matrix interface, the corresponding debonded fiber is replaced by an equivalent anisotropic inclusion taking into account the loss of stiffness due to the propagation of the crack around the interface. By iterative calculations, we are able to predict the entire non linear stress-strain curves of the composite taking into account the kinetics of local damage. The model also predicts the evolution with loading of the stiffness tensor and macroscopic anisotropy due to damage.

THERMAL RESIDUAL STRESSES IN SINGLE FIBER POLYMER COMPOSITES

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Processing methods currently used both for thermosetting and thermoplastic matrix composites involve thermal treatments at elevated temperatures. Generally, the thermal expansion properties of the fibers and the matrix are very different and therefore residual thermal stresses will always build up after cooling of the composite material. Such stresses are therefore especially large in single fiber composites, which are the typical microcomposites used in the interfacial shear strength measurement by means of the fragmentation test [1]. Residual stresses may have a great influence on the mechanical behaviour of microcomposites and therefore they should be accounted for whenever the actual fiber stresses or the actual interfacial stresses are under investigation.

In this work, fiber axial residual stresses in both thermosetting and thermoplastic single-fiber polymer composites have been experimentally evaluated by means of an original technique based on the continuous monitoring of the fragmentation test performed at various temperatures.

The difference ($\varepsilon_r = \varepsilon_a - \varepsilon_m$) between the strain at break of a single fiber in air (ε_a) and embedded in a polymeric matrix (ε_m) has been measured as a function of temperature. By considering the compressive fiber modulus (E_f) this negative strain difference has been converted into fiber compressive residual stresses (σ_r) related to the matrix thermal shrinkage after curing of the samples ($\sigma_r = E_f \varepsilon_r$). As the test temperature increased, the thermal compressive stresses resulted to decrease until a zero value was obtained, corresponding to a so called "stress free temperature". This temperature resulted equal to the curing temperature for amorphous-thermosetting matrix composites or equal to the matrix melting temperature for semicrystalline-thermoplastic matrix composites respectively. At room temperature we evaluated axial residual compressive stresses equal to 1.25 and 2.46 GPa for carbon fibers embedded in an epoxy ($T_g = 150^\circ\text{C}$) or nylon-6 matrix respectively.

The experimental results have been compared with data obtained from the Tsai-Hahn theoretical model [2]. In general a good agreement was found, but a better comparison is obtained if the temperature dependence of Young's modulus and thermal expansion coefficient of the matrix are accounted for and if appropriate volume fraction is chosen.

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THE EFFECT OF FIBER SURFACE TREATMENT
ON ITS STRENGTH AND ADHESION TO THE
MATRIX

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Realization of reinforcing fiber properties in polymer composites is promoted by the adhesion to the matrix. The surface treatment of carbon fibers is one of the ways to increase the interaction with the matrix. The changes of the fiber strength scale dependence and adhesive bond strength are results of the surface treatment.

The carbon fiber UKN-01 made from polyacrylnitril was treated by different methods and studied with the use of single fiber composites tests. These tests give information about the fiber strength scale dependence and the interfacial shear strength concurrently. It was established that all kinds of surface treatment levelled the surface defects and it is represented in changes of the fiber strength scale dependence. The same surface treatment influences the adhesion to thermofetting and thermoplastic matrices differently. So each particular system fiber-resin needs special choice of the kind and the modes of the surface treatment. It is established that fragments length distribution in single fiber composites was bimodal for untreated carbon fiber UKN and monomodal for electrochemically treated one.

An analysis of the fragments length distribution allows to hypothesize that each kind of interface interaction corresponded to the characteristic critical length. Thus this fragments length distribution reflects the nature of the fiber-resin interaction.

The deposits of the products of pyrolysis are formed by manufacture of high tensile carbon fibers. Depending on the shape and size such deposits make up special class of defects determining the low strength of carbon fiber. Criogenic surface treatment was based on the difference of the coefficients of lineal thermal expansion of the properly carbon fiber and amorphous deposits of the products of pyrolysis.

As the results we observed a removal of extraneous layer confirmed by the decrease of the diameter of fiber.

The fiber strength increased in 20 % after the criogenic treatment but the adhesion to matrix stays unchangeable.

The optimal surface modification must consist of the previous criogenic treatment and following oxydizing or another kind of treatments to increase the adhesion.

Session 7B

Determination of the Interfacial Fracture Toughness of Composites by the use of the Fragmentation test.

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Abstract

The merit of the single fibre fragmentation test as a powerful tool to measure interfacial bonding at the fibre-matrix interface in composites is now widely accepted in the composite interface community. Over these last decades the characterisation of the interface properties has been often derived from a single parameter approach based on the interfacial shear strength as proposed initially by Kelly and Tyson. The shortcomings of this analysis have been outlined by recent alternative routes such as two parameter strengths based methods, using the bond strength and the frictional resistance, as well as energetic based methods. We first review some of the energetic approaches and give some of their results. A 3-D energetic based method is then used for measuring the quality of the interface in intermediate modulus carbon fibre-epoxy systems. By means of the Energy Release Rate principle, the present approach leads to a determination of the interfacial fracture toughnesses. Comparison of the stress profiles at saturation with those obtained with conventional 1-D stress based methods are discussed.

Keywords: single fibre fragmentation test, variational mechanics, energy release rate, interfacial fracture toughness, interfacial shear strength, critical fibre length.

Abstract:

Tensile Fracture of Fibre-Polymer Interfaces

by

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We have recently shown that because of the centro symmetric geometry of the interface, matrix failure in the region of the fibre-matrix interface is strongly inhibited. This follows from our hypothesis that polymers do not fail in shear. Instead they fail in tension. (The hypothesis is supported by results from shear tests on polymers and composites, and also with the concept of the long chain nature of the polymer.) Because of this, interfaces can have strengths up to ten times greater than the polymer matrix. Failure is opening mode, in both pull out and fragmentation tests, and this arises because of the detailed geometry of the interface, which is not perfectly smooth on the atomic scale. In this paper, calculations are presented on various mechanisms of failure involving different geometries at the interface.

INTERFACIAL MICROMECHANICS OF GRAPHITE/EPOXY COMPOSITES UNDER
COMPRESSION STRESSES:
A MICRO-RAMAN SPECTROSCOPY STUDY

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Micro-Raman spectroscopy (MRS), which has the ability to measure strains in single fibers with a spatial resolution of 2 μm , is a powerful technique for monitoring the interfacial behavior in composites. In recent years, MRS has been widely used to monitor the interfacial behavior of single fiber and bulk composites under tensile stress. In addition, the technique has been used to investigate the stress concentration phenomenon in multi-fiber composites loaded in tension. However, there have been few studies to monitor the interfacial behavior of composites under compression stress using MRS. In this study, MRS was used to investigate the interfacial micromechanics of graphite/epoxy composites in compression. Graphite fibers, in compression, fail primarily in two distinct modes, i.e. a shear mode or a local buckling mode. These modes are related to the fiber structure and modulus. Multi-fiber composite were prepared using two different graphite fibers, low modulus and high modulus fibers, and used to monitor the impact of fiber failure mode on fiber/fiber interaction and the stress concentration phenomenon in the composite.

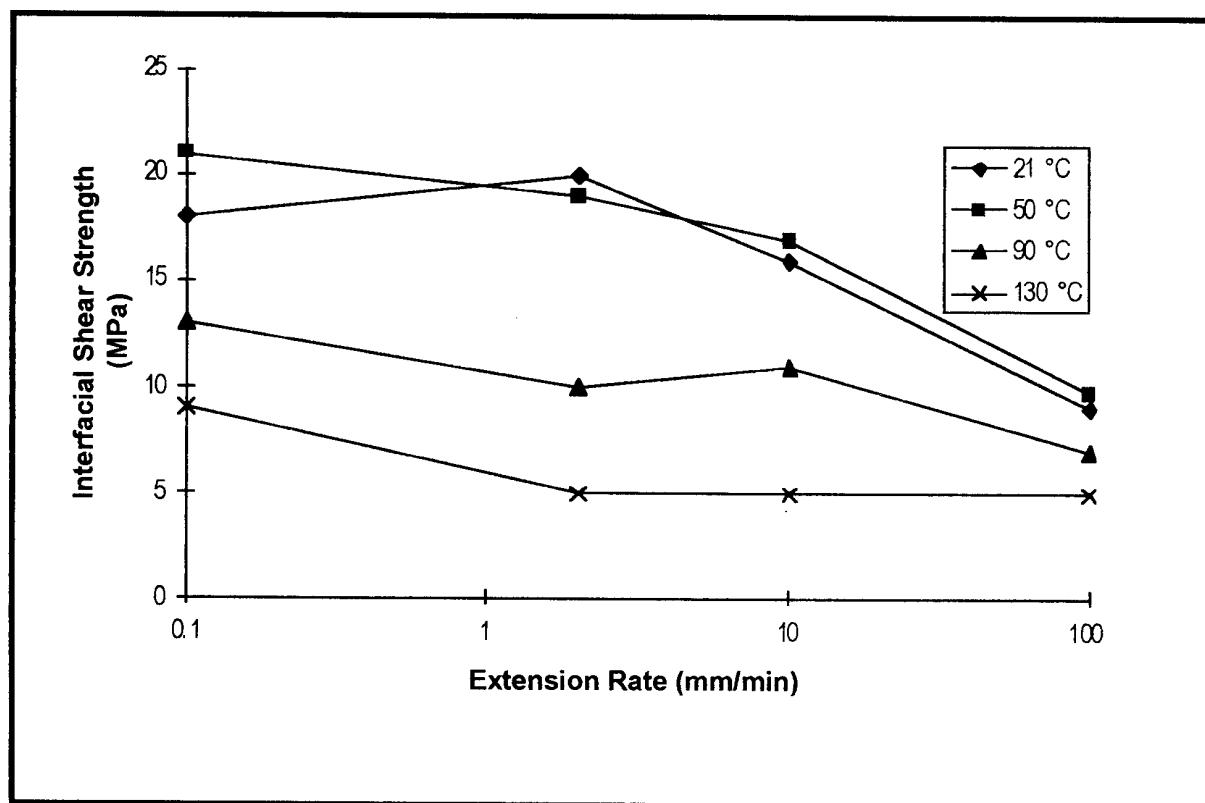
TIME AND TEMPERATURE EFFECTS ON INTERFACIAL SHEAR STRESS USING THE MICROBOND TEST

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Many matrix materials behave viscoelastically, and therefore it is reasonable to expect that the interfacial shear strength (IFSS) is a rate dependent function. Using a DGEBA-base epoxy with a T_g of 115 °C, we conducted a series of experiments to measure the IFSS achieved with a polyaramid fiber. Microbond tests were conducted over three orders of magnitude of extension rate (10⁻¹ mm/min to 10² mm/min) and a range of temperatures (21 °C - 130 °C). The results are presented below.

The extension rate below T_g produces more of an effect than near or above T_g , where the IFSS seems to be unaffected by testing rate. We analyze these data using an exponential breakdown model, and also a model due to Piggot where matrix modulus is shown to increase drastically with increasing strain rate.



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The Role of the Interface in the Toughness of Polypropylene-Glass Composites

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It has been established that there are five possible energy absorbing mechanisms for discontinuous fiber reinforced composites. These include fiber debonding, fiber pullout, fiber breakage, matrix cracking and matrix deformation. Because of the typically random orientation of fibers in these systems, it has been difficult to develop an experimental approach to determine which of these contributions play a dominant role and which play only a secondary role in measured in-plane toughness values. In an effort to address this issue, a hybrid type of specimen has been developed which involves embedding one pultruded sheet of polypropylene-glass longitudinally oriented in the center of a compression molded polypropylene bar. This specimen is then notched and tested in either Izod impact or in tensile testing. This type of specimen obviates any questions associated with fibers transverse to the applied stress, and hence provides the basis for the desired experimental approach.

Experimentally, interface strength was varied through the addition of maleic anhydride grafted polypropylene, allowing determination of the debonding and fiber breakage contributions. The pullout contribution was determined through varying fiber length. Matrix contributions were determined by changing the molecular weight of the polypropylene matrix, which changes matrix toughness by a factor of three.

Preliminary experiments thus far suggest that for maximizing impact strength in specimens with a poor fiber matrix interface there is an optimum fiber length of approximately 0.75 in., corresponding to the fiber length at which pullout predominates over fiber breakage. At longer lengths fiber breakage becomes widespread and impact strength is reduced. In specimens with a good interface, impact strength increased continuously with fiber length. Examination of these specimens suggests that delamination of the prepreg tape was the dominant energy absorbing mechanism, and hence the longer the tape, the greater the impact strength. When adhesion between the prepreg tape and the matrix was improved, delamination was suppressed and impact strength no longer increased with fiber length.

Session 8

AN EXPERIMENTAL AND NUMERICAL INVESTIGATION INTO THE INFLUENCE
OF FIBRE/MATRIX ADHESION ON STRESS ENHANCEMENT IN CARBON/EPOXY
MICROCOMPOSITES

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The unidirectional strength of fibre-reinforced composites has always been an important issue in composite science. However, the various theories which have been developed over the years to predict the unidirectional strength of composite materials are still inadequate. For example, the present theories fail to describe the influence of the fibre/matrix adhesion on the unidirectional strength correctly. Where an increase in unidirectional strength is predicted with increasing fibre/matrix adhesion, an optimum or even a decrease in strength with increasing fibre/matrix adhesion is found experimentally [1]. One of the main reasons for the poor predictions is the lack of understanding of stress enhancement in the fibres adjacent to a fibre break. Since it has been impossible to directly measure the stress concentration factor, until now this stress concentration factor has been calculated analytically, using numerous assumptions, or by finite element analysis. Recent developments in Laser Raman spectroscopy, however, make a direct measurement of stress enhancement in fibres adjacent to a fibre break possible. It has been shown that by monitoring the strain-sensitive Raman peak of certain fibres, information about its strain, and hence stress, can be obtained [2].

In this paper, Laser Raman spectroscopy is used to investigate the stress concentrations in fibres adjacent to a fibre break. Use is made of multi-fibre microcomposites containing several parallel aligned carbon fibres embedded in an epoxy matrix [3]. Recently it has been shown that such multi-fibre microcomposites are very well suited to study the influence of fibre/matrix adhesion on fibre-fibre interactions (read: stress concentrations) [3]. In order to study the influence of fibre/matrix adhesion on the stress concentrations in the microcomposites, two types of carbon fibre have been used, namely untreated (TENAX HM-40) and surface treated (TENAX HMS-40) carbon fibre. The strain-sensitive 2660 cm^{-1} peak is used to measure the fibre strain. For both fibre/matrix adhesion levels the stress concentration factor is evaluated at various inter-fibre spacings. Furthermore, in order to obtain a better understanding about the stress state in the fibres and the stress transfer via the matrix, a comparison of the experimental data with 3-D finite element calculations is made.

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INTERFACIAL MEASUREMENTS IN CARBON FIBRE EPOXY COMPOSITE TOWS USING THE TECHNIQUE OF LASER RAMAN SPECTROSCOPY

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ABSTRACT

A number of single fibre test methods have been employed over the last thirty years to assess the interfacial shear strength between fibre and matrix in composite materials. The most important of these are the pull-out test, the fragmentation test and the micro indentation test. In spite of the apparent simplicity of these tests, large discrepancies exist between the results of different tests on the same fibre matrix system, and between results from different laboratories using the same material system. This lack of reliability of micro mechanical test methods can be attributed to problems related to the experimental procedure and to the data reduction schemes employed to derive values of the interfacial strength.

The technique of Laser Raman Spectroscopy allows measurement of the stress-strain characteristics in individual fibres at the microscopic level. It can be applied to all composites provided the matrix is reasonably transparent and the fibres possess a high degree of crystallinity. Thus fibres such as carbon or aramid can be used as internal strain gauges in the composite material they reinforce. This technique enables the examination of single fibre model composites and the more complex phenomena found in a multi-fibre composite.

In continuous fibre reinforced polymeric composites, fibre failure produces a stress concentration in adjacent fibres over some distance, which is directly associated with the ineffective length. The ratio of axial stress in a fibre adjacent to a broken fibre to the stress at infinity is called the stress concentration factor K_r . This is directly related to the interfibre distance, the fibre and matrix properties, the number of broken fibres and the transfer length L_t . Since the latter depends on the strength of the fibre/matrix bond, it follows that the fracture characteristics in composites can be modified by control of the interface. The stress concentration factor is normally associated with fracture propagation in both the matrix and the surrounding fibres. It should therefore be included as an important part of any representation of the mechanisms controlling tensile failure in a composite.

Using the Laser Raman Spectroscopy technique the stress redistribution due to fibre failure was observed in near neighbour fibres in a composite tow. This work demonstrates that it is possible to measure the interfacial shear strength by balancing the tensile and shear forces acting along the fibre-matrix interface. Values for the stress concentration in adjacent fibres as a result of fibre fracture can also be obtained.

STATISTICAL FRACTURE BEHAVIOR OF A FIBER-REINFORCED COMPOSITE CONTAINING WEIBULL FIBERS, YIELDING MATRIX, AND DEBONDING FIBER-MATRIX INTERFACE

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Toughening enhancement of fibrous composites through nonelastic, energy-absorbing mechanisms, such as matrix yielding, fiber-matrix debonding, fiber bridging and pull-out in conjunction with the statistics of fiber strength is not well understood. In this work, we study the statistical aspects of the fracture behavior of unidirectional fiber composites and model the synergistic effects of the average fiber-to-matrix yield strength, interfacial shear strength, fiber strength variability, and crack size on composite fracture, and the extent and development of the crack-tip process zone. In recent work, we have developed a new technique, called the quadratic influence superposition (QIS) technique, which is computationally capable of accounting for various forms of damage, such as large numbers of random breaks, matrix yielding, and fiber-matrix debonding. Combining the influences of matrix plasticity, notch length, and fiber-matrix debonding on the Mode I fiber stress distribution, we have shown that the matrix region flanked between the last broken fiber and the first surviving fiber, increases approximately linearly with applied load. Also the remote stress required to initiate yielding decreases with square root of crack size. In this work, we examine crack extension by fiber fractures at random flaws and development of plastic and debonding zones in Monte Carlo simulations of the fracture process. Our Monte Carlo tensile "experiment" involves assigning Weibull fiber strengths and using the new QIS technique to calculate distributions everywhere at every stage in the failure process. In a recent, similar Monte Carlo study, we showed that fiber strength variability manifests in a nonlinear failure composite response from ductile-to-brittle like. In the present work, we also account for contributions to toughening from debonding and plastic deformation. These irreversible mechanicsms tend to reduce the crack-tip stress concentrations, yet increase the length scale of the overstressed region. The results of this analysis provide insight into the relationship between the dominant failure mechanisms, crack size, and applied load, and the microstructure, and point out where trade-offs may exist in achieving toughness versus strength, both of which can improve statistical features.

A NEW EVALUATION METHOD OF FIBER/RESIN INTERPHASE BY USING FIBER STRAND

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ABSTRACT

The mechanical properties of the fiber/resin interphase affect macroscopic mechanical properties of composite materials as well as fiber and resin. The adhesion between fiber and resin is caused by oxidation in carbon fiber, for example, therefore we have investigated the effect of oxidation treatment on adhesion of carbon fiber /epoxy resin interphase with single filament embedded tensile test. In preparation of the specimen for single filament embedded tensile test, the single filament has to be pulled out from a strand. In the case of sized strand, however, it is difficult to take the filament out of a strand, because sizing agent forms polymeric thin layer around strand. Even if filament can be pulled out from a sized strand, the sizing agent on the surface of filament come off in places. Then single filament embedded tensile test is not suitable for evaluating the interfacial properties with sizing agent.

We propose a new evaluation method by using strand with sizing agent. In this method, two types of tests are employed; strand embedded tensile test and strand impregnated resin tensile test. Strand embedded tensile test and strand impregnated tensile test were designated by type E and type I, respectively. In this investigation, interfacial transmissibility is used as an index of adhesion in fiber/resin interphase. The concept of interfacial transmissibility is originally proposed for single filament embedded tensile test. The type E specimen can be regarded three regions which are impregnated strand region, resin region and interphase region around impregnated strand. In determination of interfacial transmissibility strain of impregnated strand in type E test is needed, however the strain can not be measured directly, so that types E and I tests fracture of fiber in impregnated strand are recorded by using Acoustic Emission analysis system. When the numbers of events of type E equal to that of type I, strain of impregnated strand of type E is assumed to be equal to strain of type I specimen in this evaluation method. Finally interfacial transmissibility can be determined from these tests.

SIMULATION OF CRACK PROPAGATION ALONG INTERFACES IN COMPOSITE MATERIALS

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We have modeled crack propagation in a 2-D composite of hexagonal grains, with each linear segment of grain boundary having randomly assigned critical normal and shear stress intensity factors for crack growth (i.e., random "strength"). In the simulation, an initial crack was placed in the material and a loading condition (e.g. simple tension along some particular axis) was chosen. The configuration of the crack, which was confined to the bonds of the honeycomb lattice defined by the grain boundaries, was determined as a function of the magnitude of the load. The stress field for each crack configuration was calculated using an efficient new pseudotraction superposition technique for linear elastic materials in plane stress or plane strain. The parameters that we varied are (1) the configuration of the initial crack, (2) the loading condition (e.g. the orientation of the axis of simple tension), and (3) the strength distribution of the interface.

INDEX

Name	Session
Adams, J.	8
Alon, D.	3A
Ambrustolo, M.	3A
Amendola, E.	1A
Amer, M.S.	7B
Amitay-Sadovsky E.	P2
Amouroux, J.	P2
Aranguren, M.I.	P1
Arbouzov, V.	P1
Arefi-Khonsan, F.	P2
Arslanov, V.V.	P1
Asloun, E.M.	4B
Asp, L.E.	6A
Attias, A.J.	2A
Badyal, J.P.S.	P2
Baillie, C.	P2
Bak, G.W.	P2
Baker, A.A.	P2
Banhegyi, G.	P1
Bannister,D.J.	P2,P2
Baptiste, D.	7A
Bardyshev, I.I.	P2
Bartos, P.J.M.	P1
Baumgard, K.D.	P1
Beck, A.J.	3A
Beckert, W.	6B
Bellucci, F.	P1
Bennett, J.A.	6A
Berglund, L.	6A,P1
Bernardo, C.A.	P1,6B
Beyerlein, I.J.	8
Bledzki, A.K.	P1
Bloch, B.	2A
Bradley, W.L.	6A
Burghoff, M.	P1
Burton, K.J.	8
Buxton, A.L.	P2
Caramaro, L.	4B
Cervenka, A.J.	P2
Chabert, B.	P1,4B,P1
Chapel, J.P.	P1
Chatawanich, C.	6A
Chate, A.	P1
Chawla, K.K.	Opening
Cherevatsky, A.S.	P1
Choe, C.R.	4B
Chohan, V.	4A
Cohen, Y.	1A,P2
Coleman, P.G.	P2
Connell, M.E.	3B
Copponeix, T.J.	7B
Cossins, S.L.	3B
Cros, B.	P1
Cross, W.M.	3B,P1
D'Agostino, R.	P1

Dayan, H.	P1
De Saxce, G.	P1
Denault, J.	4B
Desaeger, M.	7B
Detassis, M.	7A
DiBenedetto, A.T.	Opening,P2
Dirand, X.	P1
Diwanji, A.P.	P1
Dorfman, S.	1B
Drzal, L.T.	2A
Duchet, J.	P1
Ducso, C.	P1
Dwight, W.D.	P1,3B
Dzenis, Y.A.	4B
Eisenberg, A.	2A,P1
Escoubes, M.	P1
Evlampieva, S.E.	P1
Fabri, L.	P2
Fakirov, S.	1A
Fambri, L.	P2
Faverolle, F.	2A
Favre, J.P.	Opening
Fiedler, B.	4A
Fitoussi, J.	7A
Forkel, K.	P1,2B,P1
Fracassi, F.	P1
Fuks, D.	1B
Gabbitas, B.	8
Gagina, I.A.	P1
Galiotis, C.	8,4A,P2
Gamstedt, K.	P1
Garbassi, F.	1A
Gati, A.	P2
Gauthier, R.	P1
Geller, Boris	P2
Gerard, J.F.	P1,4B
Ghorbel, I.	1B
Giannotta, G.	1A
Gietzelt, T.	P2
Gonon, L.	4B
Gonzalez-Chi, P.I.	P2
Gorbatkina, Yu. A.	4A,P1,P1
Gurvich, M.R.	P2
Grundke, K.	P2
Grynszpan, R.I.	P2
Guillemenet, J.	4B
Gundel, D.B.	1B
Guo, G.	7A
Gutman, E.M.	P2
Hamada, H.	P1,P2,P2,P2,P2,P2,P2,8
Hammer, C.O.	P1
Hampe, A.H.	P1,4A
Hana, K.	P2,P2,8
Harper, J.F.	P2
Heppenstall-Butler M.	4B
Herszberg, I.	P2
Hilaire, B.	P1
Hirai, Y.	P2
Hjertberg, T.	2A
Hofste, J.M.	P1
Huang, Yu. D.	2B
Huff, N.T.	P1

Hunsiger, J.J.	P1
Ikuta, N.	P1,P2,3A
Irzhak, V.I.	1A,P1
Ivanova-Mumjieva, V.G.	P1,4A
Jacobasch, H.J.	P1,P2,P2
Janicki, J.	P2
Janik, H.	P1
Janowski, F.	P2
Joly, C.	P1
Jones, F.R.	2A,3A
Kageyama, K.	7A
Kalashnikova, I.V.	P1
Kalinka, G.	P1
Kaplan, W.D.	2B
Karbhari, V.M.	P2
Kastner, R.	P1
Kaynak, A.	P2
Kellar, J.J.	P1,3B
Kendall, K.	5
Kerans, R.	Opening
Kettle, A.P.	3A
Khazanchi, A.C.	3A
Khodakovskaya, R.	P1
Khodakovsky, M.	P1
Kimpara, I.	7A
Kiselev, M.R.	P2
Kitagawa, K.	P1
Kiyosumi, K.	P2
Klein, J.	5
Klemburg-Sapicha, J.	2A
Koczak, M.J.	1B,7B
Korabelnikov, Y.	7A
Kotaki, M.	P2,P2,P2,P2,8
Krishnamoorthy, P.R.	P1
Kryszewski, M.	P2
Kuzub, L.I.	1A
Lauke, B.	6B
Le Bars, O.	2A
Leistner, A.	P1
Lemstra, P.J.	P1
Leong, K.H.	P2
Levi, E.	P1
Li, Z.W.	7A
Liu, Y.C	4A
Lifshits, A.	P1
Linek, M.	P2
Lohner, T.	P1
Lourie, O.	P2
Lovell, A.P.	P2
Luhr, J.	P2
Lustiger, A.	7B
Ma, S.	P1
Maeder, E.	P2,P2,3B
Mahy, J.	3B
Mai, K.	P2
Majumdar, B.	1B
Manevitch, L.I.	P2
Marcovich, N.	P1
Marom, G.	P2
Marotzke, C.G.	4A,6B
Marston, C.	4A,8
Matveev, V.V.	P1

Maurer, F.	P1,3B
Meijer, H.	P1
Meurs, P.	P1
Michel, V.	P1
Michiels, S.J.	P2
Migliaresi, C.	P2,7A
Miracle, D.B.	1B
Mittelman, A.	P2
Monetta, T.	P1
Morii, T.	P2
Moschiar, S.M.	3A
Moshev, V.V.	P1
Mullejans, H.	2B
Murano, Y.	P2
Muravin, D.K.	P2
Nairn, J.A.	P1,4A
Nakanishi, Y.	P2
Nardin, M.	P1,P1,4B,6B
Nicodemo, L.	P1
Nicolais, L.	1A
Nihlstrand, A.	2A
Nishiyabu, K.	P2
Occhiello, F.	1A
Ogarev, V.A.	P1
Ohlson, K.G.	P2
Ohsawa, I.	7A
Opella, K.C.	P1
Oshmyan, V.G.	P2
O'toole, L.	3A
Paipetis, Alkis	P2
Paiva, M.C.	P1,6B
Paris, D.	P1
Park, M.	4B
Partridge, I.K.	6A
Pavlenko, A.V.	P2
Pays, M.F.	P1
Pegoretti, A.	P2,7A
Peijs, T.	P1,P1,8
Pennings, A.J.	P1
Phoenix, S.L.	8,8
Piggott, M.R.	7B
Pisanova, E.V.	P2,P2
Piven, N.	P1
Podgaiz, R.	P2
Pritykin, L.M	P1
Puchkov, L.V.	P1
Qi, B.	P2
Qiao, L.	6B
Ramaswamy, P	P1
Ramos, A.	6B
Rao, K. J.	P1
Rashkovian, I.	7A
Reboredo, M.M.	P1,3A
Redlich, B.	P2
Rein, D.M.	1A,P2
Remond, Y.	P2
Rolle, S.	P1,P1,2B,
Roman, I.	P2
Rublenko, D.I.	P1
Rudoy, V.M.	P1
Ruhle, M.	2B
Rutkowska, M.	P1

Saalbrink, A.	P1
Sadovsky, J.	3A
Salmon, L.	P1
Schadler, L.S.	7B,7B
Scheer, R.J.	P1
Schneider, S.	P1
Schreiber, H.P.	2A
Schreurs, P.	P1
Schulte, K.	P1,4A
Schultz, J.	P1,4B,6B
Schutte C.	4A
Schwartz, P.	7B
Sharpe, L.H.	Opening
Seetharamu, S.	P1
Sherman, D.	2B
Short, R.D.	3A
Shul, G.S.	P1
Silverstein, M.S.	3A
Simon, F.	P2
Slivka, M.	7B
Slusarczyk, C.	P2
Spange, S.	P2
Stanford, J.L.	P2
Stern, T.	P2
Stodolski, R.	2B
Straub, A.	7B
Suliaeva, Z.P.	P1,4A
Sun, W.X.	2B
Suzuki, T.	7A
Tatoulian, M.	P2
Thaumaturgo, C.	1A
Thiel, H.	P2
Thominette, F.	P1
Thongpin, C.	P2
Tregub, A.	P1,P2
Tregub, I.	P2
Tripathi, D.	2A
Tsagaropoulos, G.	2A
Tu, M.	P2
Turmel, D.J.P.	6A
Turusov, R.A.	P1,P1
van den Heuvel, P	8
Varma, K.B.R.	P1
Vaykhansky, L.E.	1A,P2
Vazquez, A.	3A
Verdu, J.	P1
Verpoest, I.	7B
von Lacroix	P1
Wacker, G.	P1
Wagner, C.	P2
Wagner, H.D.	P2,P2,P2,P2,7A
Wang, J.S.	2B
Warrier, S.	1B
Wei, Y.Z.	2B
Weinberger, T.	P2
Wihsmann, F.G.	P1,P1,2B
Williams, D.E.	7B
Williams, R.	P2
Winter, R.M.	P1,3B
Wittich, H.	P1
Wlochowicz, A.	P2
Wood, C.	6A

Wu, H.F.	P1
Wu, X.D.	P2
Yilmazer, U.	P2
Yokoyama, A.	P2
Young, R.J.	P2,P2,P2,4B,6A
Zaslavsky, N.	P1
Zhandarov, S.F.	P2,P2
Zhang, Z.Q.	2B
Zhou, X.-F.	P2
Zhu, M.	P2